

CHEMICAL ABSTRACTS

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No. 4

1—APPARATUS

C. G. DERICK

Heat economy in the chemical industry. GERMER. *Chem. App.* 9, 223-4(1922).—Three types of boiler-feed water meters are briefly described. J. H. MOORE

Decision of the testing commission of the technical committee for chemical apparatus. Section for laboratory apparatus. H. RABE. *Z. angew. Chem.* 35, 629(1922).—The proposed specifications (cf. Bechergläser, *Ibid* 35, 142, 145(1922)) are confirmed except as follows: *Beakers*.—The diam. of the flat part of the bottom is to be $\frac{3}{4}$ of the outside diam. *Crystg. dishes*.—The bottoms are to be like beakers. *Flasks, round with short, narrow neck*.—The 4 and 6 l. sizes are omitted; the 100–1000 cc. sizes are to have ring necks. *Flasks, fractionating*.—50 and 100 cc. sizes are to be round. *Flasks, Erlenmeyer*.—The 250 cc. size is replaced by 200 and 300 cc. sizes and the dimensions of these are tabulated. *Supplement to decision*.—1: the ruling, "thermometers up to 300° are filled under pressure," is changed to read, "while the capillaries of thermometers up to 250° are air-free, they are filled under 0.1 atm. up to 300°, under 1 atm. up to 300°, and under 18 atm. pressure (abs.) up to 500°." J. H. MOORE

New device for recovering liquid solvents in chemical operations. B. MÜLLER. *Chem.-Ztg.* 46, 1061-2(1922).—Where solvents are removed from chem. products at low temp. under vacuum and recovered by passing the exhaust from the pump through condensers, diln. of the exhaust with air may be prevented by connecting the intake to the vacuum regulator into the exhaust line between the pump and condenser.

J. H. MOORE

Explosion buret. A. KRIEGER. *Chem.-Ztg.* 46, 1060-1(1922).—The app. is shaped like the link of a chain, 40 cm. long and 8 cm. across, outside. The measuring buret is attached to a neck at the top and a leveling bottle to 1 at the bottom. The inside diam. of the arms is such that the H₂O or Hg stands about 10 cm. above the bottom at the time of the explosion, which is very quiet.

J. H. MOORE

The calibration of gas-flow meters. J. OBERMILLER. *Z. angew. Chem.* 35, 659-62(1922).—A description of a method for checking up the accuracy of small meters, with 2 cuts showing the arrangement of the app. Both sizes of the Riesenfeld meter (*Chem.-Ztg.* 42, 510(1918)) were checked and the results given. J. H. MOORE

Appliances for moving liquids in chemical plants. A. K. FISCHER. *Chem. Age* (N. Y.) 30, 501-4(1922).—An illustrated description of 9 typical arrangements of the steam-jet pump or siphon and eight layouts of the air-jet lift using compressed air.

A. C. LANGMUIR

A simple automatic dropping and constant level contrivance for use in washing with acids. F. REIMANN. *Biochem. Z.* 133, 112-13(1922).

F. S. HAMMETT

An apparatus for preparing dry powders of dissolved or suspended thermolabile substances. DAG SALOMONSON AND H. V. EULER. *Arkiv. Kemi, Mineral. Geol.* 8, No. 24, 1-3(1922).—With this app. the liquid to be dried is dispersed into a very fine mist by an atomizer arrangement, and dry CO₂ at a temp. of 70° is blow against this mist. The solid matter is deposited on the wall of the collecting vessel as a fine powder. Unheated CO₂ is used for the atomizing.

D. E. S.

An apparatus for the measurement of specific gravity of gases in small quantities. ALFRED BLACKIE. Dept. of Sci. Ind. Research, Fuel Research Board, *Tech. Paper* No. 5, 6 pp. (1922).—A column of the gas under test is balanced against an equal column of air, and the difference in pressure is measured by a Chattock tilting gage. Means for maintaining a uniform temp. and measuring it accurately are incorporated. The accuracy of the app. is about 0.5% for gases with sp. gr. from 0.4 to 0.8 (air = 1), and 1.5 l. of gas is sufficient for 2 complete measurements. D. E. S.

Two new pieces of laboratory apparatus. S. SOMAZZI. *Z. deut. Oel-Fett-Ind.* 42, 726-7 (1922).—(1) A somewhat intricate glass app. with ground joint for rapid extns. is described; the app. has been adopted for the detn. of impurities by the Italian Commission for standard methods of analysis. (2) S. describes a double-walled drying oven for const. temp. of 103° which automatically regulates the gas supply by closing and opening the latter by a rising or falling column of Hg, the gas being lighted by a pilot flame from a sep. gas supply. P. ESCHER

An oven for crucibles. W. MASON. *Chem.-Ztg.* 46, 1080-1 (1922).—A description with 7 cuts. J. H. MOORE

Electric hot-plate with socket. ANON. *Chem.-Ztg.* 46, 1081 (1922). J. H. M.

The absorption of gases by chabazite (NÄCKEN, WOLFF) 8. Evaporation (WEBER) 13.

Acetylene generator. O. J. WARMAN. U. S. 1,436,128, Nov. 21.

Apparatus for measuring carbon dioxide in gaseous mixtures. J. W. McNAIRY. U. S. 1,436,273, Nov. 21. Gas to be analyzed is supplied under pressure through a casing around an inlet valve of the absorption chamber.

Apparatus for measuring carbon dioxide in gaseous mixtures. C. VAN BRUNT. U. S. 1,436,219, Nov. 21. An absorption reagent such as $\text{Ca}(\text{OH})_2$ and H_2O is circulated between a supply tank and a reagent chamber which supplies reagent to an absorption chamber where the gas under test is treated.

Apparatus for drying materials by steam heat and air currents. H. BENTZ. U. S. 1,436,142, Nov. 21.

Apparatus for continuous production of ether. E. A. BARRET. U. S. 1,436,332, Nov. 21. The app. comprises a tubular alc. heater from the top of which alc. vapor is led to the base of a mixer where it is brought into contact with hot H_2SO_4 poor in ethylsulfuric acid. Connections lead the product rich in ethylsulfuric acid from the head of the mixer to a boiler. Ether vapor is distd. from the boiler and acid freed from ether is returned from the boiler to the mixer.

Ozone generator. H. B. HARTMAN. U. S. 1,437,302, Nov. 28. The generator is adapted for use with H_2O -purifying app. and comprises a casing with an air inlet at its top and ozone outlet at its bottom sealed against the entrance of H_2O .

Electric ozone generator. H. B. HARTMAN. U. S. 1,436,251, Nov. 21.

Electric water heaters. S. G. CRANE. U. S. 1,437,383-4, Nov. 28.

Muffle furnace. A. McD. DUCKHAM. U. S. 1,436,582, Nov. 21. An annular muffle furnace is built with a traveling platform to which material may be supplied and from which the residue of the material may be removed without interrupting the operation of the furnace.

2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

Heinrich Rubens. WILHELM WESTPHAL. *Naturwissenschaften* 10, 1017-20 (1922).—An obituary. Rubens and the art of experimentation. E. REGENER. *Ibid* 1021-4.—Biographical. Rubens and the Maxwell theory. G. HERTZ. *Ibid* 1024-7. The discovery of the long-wave radiation of mercury vapor by Rubens. O. VON BAERYER. *Ibid* 1027-30. Rubens and the quantum theory. J. FRANCK AND R. POHL. *Ibid* 1030-3. The importance of the work of Rubens for the Planck radiation formula. G. HERTNER. *Ibid* 1033-40. List of works published by Rubens. ANON. *Ibid* 1038-40. C. C. DAVIS

The protection of brass weights. J. J. MANLY. *Phil. Mag.* 44, 948-50 (1922).—A modification of a method first used by Faraday to protect Fe from rust, is applied to brass wts. The wts. are tooled to remove tarnish, polished, heated in a semi-luminous gas flame until nearly red hot and then plunged into boiled linseed oil and left to cool. After removal and washing with turpentine and polishing with old linen, the wts. are adjusted, standardized and put into use. Modern coal-gas contains too much S for direct heating, and it was found necessary to use a vitreous crucible with lid or a muffle. After cleansing and polishing each wt. is covered with a thin layer of linseed oil and then placed on a 3-point porcelain support in the crucible or muffle just above a layer of asbestos. Heat is applied until a golden tint is observed, when the heating is ended and after cooling an even coating is obtained which weighs about 0.05 mg. per sq. cm. of surface. S. C. L.

The discharge of air through small orifices and the entrainment of air by the issuing jet. J. S. G. THOMAS. *Phil. Mag.* 44, 969-88 (1922). S. C. L.

Natural convective cooling in fluids. A. H. DAVIS. *Phil. Mag.* 44, 920-40 (1922).—The consideration of natural convective cooling is extended from that of gases to fluids in general. A more rigid theoretical treatment leads to the same simplified general formula as previously deduced for long horizontal lengths of wire of diam. d : $H/k = F(c^2gd^3a\theta/k^2)f(cv/k)$, in which H is the heat loss per unit length of wire per degree temp. excess, k is the thermal cond. of the fluid, c the heat capacity per unit vol. of fluid, g is acceleration due to gravity, a is the coeff. of reduction of density per 1° rise in temp., θ is the temp. excess of the body, ν is the kinematical viscosity of the fluid. When cv/k is const., $H/k = F(d^3gac/k\nu)$. The exptl. arrangement consists of a Wheatstone bridge set up to measure the energy supply necessary to maintain a measured temp. difference between a wire and the general body of the liquid. The elec. energy is detd. by the current through the wire and its resistance, which latter also det. its temp. Measurements were carried out for a gas, for toluene, CCl_4 , aniline, olive oil, and glycerol. The results plotted on a curve with H/k as ordinates and $gd^3ac/k\nu$ as abscissas fall on a smooth curve for all the different fluids, showing H/k to be a function of the other expression as given in the formula above. S. C. LIND

The full effect of variable head in viscosity measurements. F. M. LIDSTONE. *Phil. Mag.* 44, 953-5 (1922).—Additional corrections in the treatment of the variable head in viscosity measurements (cf. *C. A.* 16, 1524). S. C. L.

Properties of salt solutions. W. L. BADGER. *Chem. Met. Eng.* 27, 932-3 (1922).—Curves for (1) soly.-temp., (2) d.-temp., (3) sp. heat-temp., (4) excess boiling point-pressure, (5) d.-soly., (6) soly.-% solids, and (7) soly.-% satn. are given for NaCl solns. I. A. PRIDGON

Membrane equilibria. W. E. GARNER. *Brit. Assoc. Advancement of Sci.*, 4th Report, 1922, 114-21.—An historical and crit. review of the work of Ostwald, Haber and Klemensiewicz, Loeb, Beutner, Donnan, Harris and others. JEROME ALEXANDER

Solubility of barium selenate. J. MEYER AND W. FRIEDRICH. *Z. physik. Chem.* **102**, 369-87 (1922).—The equiv. conds. of solns. of Na_2SeO_4 and of K_2SeO_4 have been detd. at 5, 18, 25, 35 and 50° between the dilns. $v = 2$ and $v = 2048$. From the results the ion-conductance of SeO_4^{2-} at 18 and 25° has been calcd. for the different concns. At infinite diln. the ion-conductance = 64.57 at 18° and 74.24 at 25°. The temp. coeffs. of the SeO_4 ion at infinite diln. are resp. $c = 210 \cdot 10^{-4}$ and $c' = 49 \cdot 10^{-6}$ ($\kappa_{12} = \kappa_{12}[1 + c(t_1 - t_2) + c'(t_1 - t_2)^2]$, where κ is the measured cond.). The transference nos. of the SeO_4 ion in K_2SeO_4 , Na_2SeO_4 and BaSeO_4 at 18° are, resp., 0.500, 0.598 and 0.540. From the cond. data the soly. of BaSeO_4 is 82.5 mg. per l. H. J. C.

The molecular theory of solution. II. S. C. BRADFORD. *Phil. Mag.* **44**, 897-904 (1922); cf. *C. A.* **14**, 673.—Theory of soln. is considered through the mol. forces in solvent and solute and between the two latter. Soln. equil. is treated as a dynamic state and an equation of force (f) for a particle of a solid escaping into pure solvent is developed: $f = (M^2_w/r^4_{ws}) - 2(M_w \times M_s/r^4_{ws}) + (M_s/r^4_{ss})$, in which M is mol. force, w and s as subscripts refer to solvent and solute resp., and r is the distance between mol. centers. Osmotic pressure can be directly related to this force also, but since osmotic data are much more meager than those of f , p. lowering, a relation is developed between abnormal lowering for electrolytes and the surface tension increase. A table for NaNO_3 , KNO_3 , Na_2SO_4 , K_2SO_4 , Na_2CO_3 , K_2CO_3 , NaCl , and KCl shows a remarkable agreement at different concns. for the increase of f , p. lowering beyond normal and the surface tension $\times 0.64$, showing $\delta\Delta = 0.64 \delta\sigma$. S. C. LIND

Dissociation of hydrogen sulfide, sodium sulfide and sodium hydrogen sulfide in aqueous solutions. K. JELLINEK AND J. CZERWINSKI. *Z. physik. Chem.* **102**, 438-79 (1922).—Measurements of the lowering of the f , p., the cond. (at 0°, 18° and 25°), and e. m. f. (at 10.5°) have been carried out with aq. solns. of Na_2S and NaHS over a wide range of concns. The concns. of the different mol. species present in the hydrolytic equil. of Na_2S and NaHS have been ascertained for different total concns. of these salts. The degree of hydrolysis of Na_2S at 0° varies from 0.805 at an equiv. concn., $c = 0.1$ to 0.46 at $c = 2.85$. The heat of dissocn. of the HS ion is probably 13000 cal. The 2nd dissoc. const. of H_2S is 2×10^{-15} at 0°. The large difference between the 2 dissoc. const. of H_2S ($k_1 = 10^{-7}$ at 0°), together with its heat of dissoc., point to a marked asymmetrical structure of the H_2S mol. The ion-conductances of the HS and S ions at 0° are, resp., 42.5 and 115. The temp. coeff. of the conductance of the former ion is 0.015 to 0.018 at 18°. New detns. of the soly. product of CuS , PbS and AgS give the values 3×10^{-12} , $1.4 - 5.0 \times 10^{-16}$ and 3×10^{-19} , resp. The high value for the soly. product of PbS points to the existence of a more sol. modification of PbS .

H. JERMAIN CREIGHTON

Volume change on dissolution of thallous sulfate. FUSAO ISHIKAWA. *J. Chem. Soc. Japan* **43**, 576-98 (1922).—The vol. change, Δv , of Tl_2SO_4 was detd. by 2 different methods at 30°: (1) by means of the expression $\Delta v = \left[\left(\frac{dE}{d\pi} \right)_{T,e} \right]_A - \left[\left(\frac{dE}{d\pi} \right)_{T,e} \right]_B$

where $\left(\frac{dE}{d\pi} \right)_A$ is the change of e. m. f. of cell A ($\text{Ti-Hg} | \text{satd. soln. of } \text{Tl}_2\text{SO}_4 \text{ with}$

solid $|\text{Hg}_2\text{SO}_4 | \text{Hg}$) under different pressures and $\left(\frac{dE}{d\pi} \right)_B$ is that of cell B ($\text{Ti-Hg} | \text{satd. sol. of } \text{Tl}_2\text{SO}_4 \text{ without solid } |\text{Hg}_2\text{SO}_4 | \text{Hg}$). Both cells are at const. temp. T , and in the condition following passage of the same elec. current e . Measurement shows that $\left[\left(\frac{dE}{d\pi} \right)_{30^\circ} \right]_A = 0$, and $\left[\left(\frac{dE}{d\pi} \right)_{\pi=1} \right]_B = +0.00001298$ v/pressure. Thus

Δv (for 1 g.) = -0.04906 cc. (2) By the sp. vol. method, using the formula $\Delta v = +V_{c_1} (1 - c_1) \left(\frac{dV_c}{dc} \right)_{c=c_1} - V_{c_1}$, where V_{c_1} is the sp. vol. of the soln. when c the concn. =

1, and V_s is the sp. vol. of the solid. (Cf. Cohen and Moesveld, *C. A.* 13, 2787.) This method gave $\Delta v = -0.05407$ cc./g. Thus the value obtained by the elec. method is 10% smaller than that by the specific vol. method. The causes for the discrepancy, which is beyond exptl. error, are under further investigation. S. TASHIRO

Surface tension in solids. G. N. ANTONOFF. *Z. physik. Chem.* 102, 388-92 (1922); cf. *C. A.* 13, 274.—A mathematical relation has been deduced for the internal pressure (P) of solids. From the values obtained for the breaking-load of rock salt crystals it is shown that $P/p^{1/3} = 1.4$ dynes/cm.², where $p = 1/d^3$ and d is the attraction between the doublets. If the attraction between the charges is not influenced appreciably by the neighboring series (of doublets), the above value for $P/p^{1/3}$ represents the surface tension in the direction of the vertical axis. If the field is sym. in all directions to the equiv. axes, then it represents the surface tension of rock salt in all 3 directions.

H. JERMAIN CRIGHTON

Catalysis of hydrogen peroxide by ferric salts. J. DUCLAU. *Bull. soc. chim.* 31, 961-6(1922).—The results of von Bertalan (*C. A.* 14, 3183) and Bohnson (*C. A.* 15, 1244) were confirmed. The value of $K = k \times C_{H_2O_2}/C_{Fe}$ was practically const. at or $> C_{H_2O_2} = 0.003 N$ instead of 0.005 N as calcd. from the results given by Bohnson. In this equation k was detd. from $\log(C/C_0) = k(t-t_0)$. Below 0.003 N the value of k seemed to approach 0 with decreasing acidity. The variation of k is explained by assuming the essential factors in this catalysis to be the Fe^{+++} ions and the peroxide ions (HO_2). The mechanism of the reaction between the ions, as already in part verified exptly. by Bohnson, probably consists in the formation of an intermediate compd., a peroxide or acid of Fe with the formula $Fe(HO_2)$, $Fe(HO_2)_2$ or $Fe(HO_2)_3$. This compd. or ion complex would decompose instantly to form O_2 , H_2O and some Fe^{++} ions. The latter would be immediately changed to Fe^{+++} ions by the excess of H_2O_2 .

H. M. McLAUGHLIN

Chemical affinity. E. YAMAZAKI. *J. Chem. Soc. Japan* 42, 499-510(1921).—A theoretical paper. van't Hoff and Nernst's calcul. of chem. affinity does not hold in the case of a system in equil., where a chem. change will produce a certain amt. of change in work by each component in the system. Chem. affinity should not only be calcd. at const. vol., as A_v , but should also be considered at const. pressure, as A_p . The formulas developed are, $A_v = RT \ln(C_1^{n_1} C_2^{n_2} \dots / C_1'^{n_1} C_2'^{n_2} \dots) - RT \ln K_0$, $A_p = RT \ln(P_1^{n_1} P_2^{n_2} \dots / P_1'^{n_1} P_2'^{n_2} \dots) - RT \ln K_p$, where C_1, C_2, \dots are concns. of components of the original system, and C_1', C_2', \dots are those of the final system; similarly P_1, P_2, \dots , and P_1', P_2', \dots are partial pressures of the components; and n is the usual exponent indicative of the no. of atoms or mols. of a given kind involved in the equil. The relation between A_p and A_v is expressed as $A_p = A_v - (\Sigma n - \Sigma n') RT \ln RT$. S. T.

Dissociation of iodine vapor and the chemical constant of monatomic iodine. H. BRAUNE AND H. RAMSEYER. *Z. physik. Chem.* 102, 490-503(1922).—An attempt has been made to remove the discrepancy between the empirical and theoretical values for the chem. const. of monatomic I through a new detn. of the dissoci. equil., $I_2 \rightleftharpoons 2I$. The results of the investigation do not remove the discrepancy. It is pointed out that agreement between the 2 values is possible only if the exptl. quantities employed in the calcul. of the chem. const. (i. e., the change of the sp. heat of solid I with temp. and the heat of vaporization of I) are affected by unexpectedly large errors. H. J. C.

Concentric standard cells. Y. ISIMASU. *Researches Electrotech. Lab., Japan* 113, 12 pp.(1922).—A concentric standard cell, convenient for the insertion of materials and also for washing and drying the glass vessel, is designed. The constancy, temp. coeff. and the internal resistance of this form are the same as in the case of the H-form standard cell. The characteristics of recovering to the steady state in both forms of cells for an abrupt change of temp. were studied. The temp. coeffs. of both limbs were

as follows: $\delta_a = -0.000,344_1(t - 20) - 0.000,001_1(t - 20)^2$; $\delta_b = +0.000,309_2(t - 20) + 0.000,000_2(t - 20)^2$.

W. OGAWA

The electrical resistivity and its temperature coefficient of manganin. S. KUMURI AND K. SAKAMAKI. *Researches Electrotech. Lab.*, Japan 114, 10 pp.(1922).—The resistivity and its temp. coeff. of Cu-Mn alloys and the effects of other elements such as Ni, Fe, Al and Si upon them are investigated. From their exptl. results, the authors have found that a straight Cu-Mn alloy can furnish the best manganin, and that there is no need of adding other elements to manganin for the purpose of improving the resistivity and its temp. coeff. The straight Cu-Mn alloys of about 13% Mn content made in the authors' lab. have the following elec. properties: sp. resistance 45 microhm per cm.; temp. coeff. at 22.5° -0.0000348 .

W. OGAWA

The use of a triode valve in registering electrical contacts. G. A. TOMLINSON. *Phil. Mag.* 44, 870-2(1922).—Description of a set-up, which enables the detection of contact by extremely low currents, including in the valve circuit a Pt leaf contact, 3 small batteries and regulating resistance, and in the secondary circuit an instrument to detect deflection from zero in either direction. It has decided advantages over ordinary relays. Uses are suggested in the reception of feeble wireless signals, in reading the height of Hg in barometers and other instruments. Additional uses will readily suggest themselves.

S. C. L.

Magnetic rotary dispersion of certain paramagnetic solutions. R. W. ROBERTS, J. H. SMITH AND S. S. RICHARDSON. *Phil. Mag.* 44, 912-20(1922).—The magnetic rotation of the magnetic elements has been mainly observed with the D line of Na. In the present investigation aq. solns. of Ni, Co, and Fe salts have been examined in the ultra-violet region. The results indicate that the Co atom like the Fe atom can produce negative rotation but of smaller numerical value. The observed disappearance of the effect on the low-frequency side of the band may be due to the preponderance of the effect of the negative ion. Ni remains positive throughout the range observed. The results indicate that the Co atom occupies an intermediate position between Ni and Fe with reference to paramagnetism.

S. C. L.

Inorganic complex salts, crystallographic and optical study (KNAGGS) 6.

BAUER, H. Ein Jahrbuch der Chemie. Stuttgart: Francksche Buchhandlung 88 pp. M 9.60. Reviewed in *Z. Ver. deut. Eng.* 66, 64(1922).

BOLL, MARCEL and ALLARD, GEORGES. Cours de chimie (métaux et cations). Paris: Dunod.

BROWNLEE, R. B., FULLER, R. W., HANCOCK, W. J., SOHON, M. D., WHITSITT, JESSE E. Laboratory Exercises. New York: Allyn & Bacon. 250 pp.

CAVENDISH, H. Scientific Papers. Vol. 1. Electrical Researches. Edited by J. Larmour. Vol. II. Chemical and Dynamical. Edited by E. Thorpe. Cambridge: University Press. 496 pp. 120s.

CHAZEL, ARNOLD. Lehrbuch der chemie und chemischen Technologie für Handelsakademien. - I Teil. 3rd Ed. revised. Vienna: Carl Fromme. M 100.

ERNST, G. Naturkunde für Mittelschulen II Teil. Chemie. Hanover: Carl Meyer. 195 pp. Reviewed in *Chem. Weekblad* 19, 120(1922).

KRAUS, CHARLES A. The Properties of Electrically Conducting Systems. New York: The Chemical Catalog Co., Inc. 415 pp. \$4.50. Reviewed in *Chem. News* 125, 240(1922); and *Can. Chem. Met.* 6, 207(1922).

MEYER, R. Vorlesungen über die Geschichte der Chemie. Leipzig: Akademische Verlagsgesellschaft. m. b. H. 467 pp. M 200, bound M 240.

MIELI, A. Gli scienziati italiani dal medio evo ai nostri giorni. Vol. I. Part I. Rome: Attilio Nafdecchia. 236 pp. L 45. Reviewed in *Scientia* 31, 307(1922).

MURANI, O. Lezioni di termodinamica. 2nd. Ed. revised. Milan: Ulrico Hoepli.

NAGEL, OSKAR. Die Romantik der Chemie. 10th Ed. Stuttgart: Francksche Verlagshandlung.

SVEDEBERG, THE. Die Methoden zur Herstellung Kolloider Lösungen Anorganischer Stoffe. Dresden and Leipzig: Verlag von Theodor Steinkopff. 508 pp. Unbound 13s. 2d. Bound 14s. 2d. Reviewed in *Chem. News* 125, 270(1922).

SWARTS, FRED. (1) Cours de chimie organique (2) Cours de chimie inorganique. Edited by Maurice Lamertin. 3rd Ed. Revised and enlarged. Brussels: Maurice Lamertin. (1) 674 pp. 45 fr. (2) 734 pp. 50 fr. Reviewed in *Chem. News* 125, 240(1922).

Van Nostrand's Chemical Annual. 5th Ed. Revised and enlarged. Edited by John C. Olsen, New York, D. Van Nostrand Co. 900 pp. \$4.00. Reviewed in *Am. Perfumer* 17, 363(1922).

WOLSKI, PAUL. Kleines Praktikum der Kolloidchemie. 4th Ed. Dresden: Theod. Steinkopff. M 60.

3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

Remarks on the resonance and ionization potentials of helium. J. FRANCK. *Z. Physik* 11, 155-60(1922).—The lines in the extreme ultra-violet spectrum of He recently discovered by Lyman (*C. A.* 16, 3589) constitute the principal series $0.5S-mP$ of He⁺. The wave length data require that the resonance and ionization potentials be decreased by 0.8 v. A review of the work done by him in measuring these potentials convinces F. that an error was made in the interpretation of the readings of his voltmeter. The value 19.75 v. belongs to the inter-orbital transition $0.5S-1.5S$, while the value 20.55 v., which is 0.7 v. greater than the former, belongs to $0.5S-1.5S$ to which the value 21.25 v. was formerly erroneously assigned. The resonance and ionization potentials of all gases based on those of He must likewise be decreased by 0.7 v. C. C. KIESS

Spectroscopic measurement of the electron affinity of chlorine. E. v. ANGERER. *Z. Physik* 11, 167-9(1922).—A discharge tube of special design was used to exam. the hitherto unknown ultra-violet spectrum of Cl. The capillary of the tube was in shape a double cone, on one base of which was cemented a quartz lens whose focus was at the common vertex of the cones. In addn. to a discontinuous spectrum of numerous intense lines, Cl also exhibits in the ultra-violet a continuous spectrum of which the long wave limit lies at $\lambda = 3180 \pm 10\text{\AA}$. Franck has indicated (*C. A.* 16, 872) that the long wave limit of the continuous spectrum affords a measure of the electron affinity of an element. Assuming that proportionality exists between the long wave length limits and electron affinities found for I and Br, calcn. shows that the electron affinity of Cl is 89.3, in contrast to the value 119 found by Born by an entirely different method. C. C. KIESS

The dissociation of hydrogen molecules by means of excited mercury atoms. G. CARIO AND J. FRANCK. *Z. Physik* 11, 161-6(1922).—An expt. was devised which proved the correctness of the conclusion, drawn from theoretical considerations, that excited atoms colliding with other atoms impart to them the energy quanta required for chem. reactions. A quartz tube 10 cm. long and 1 cm. bore contained some Hg on the surface of which was a small float holding a metallic oxide. A side tube contg. Pd served as source of H which could be mixed with the Hg vapor. The Hg tube was

exhausted and the pressures within it were read on a MacLeod gage. By warming the tube Hg vapor was formed, and the Hg atoms were then excited by exposing them to the radiation $\lambda = 2536.7\text{\AA}$. emitted by a quartz Hg lamp. H mols. struck by excited Hg atoms are dissociated if sufficient energy is imparted to them during collision. If H atoms are produced they will reduce the metallic oxide, producing H_2O , which can be condensed in a liquid-air trap. Two oxides were successfully used— CuO and WO_3 . The pressure of the H showed a steady decrease as the excitation of the Hg vapor progressed. Furthermore the velocity of the reaction was found to depend on the pressure of H within the tube. When this reached 15 mm. a sufficient no. of collisions occurred so that the energy absorbed by the Hg no longer appeared as resonance fluorescence but was imparted to the H. C. C. KRESS

The problem of the model of the hydrogen molecule. A. BUCKEN. *Naturwissenschaften* 10, 947-8(1922); cf. *C. A.* 16, 2806.—Born's contention that any proposed structure of the atom must be based on adiabatic principles (cf. *C. A.* 16, 4126) is considered to be not well founded. According to Herzfeld (cf. *C. A.* 16, 4114) the potential energy set free in the collision of 2 atoms must be absorbed by a 3rd atom or a mol. if a stable mol. is to result. These collisions need not occur simultaneously, and only for the 1st is the adiabatic hypothesis applicable, e. g., in the transformation of unstable He into its stable modification. In general the adiabatic hypothesis is deemed valid only for changes occurring at rates much slower than those involving quanta. The validity of any model must be detd. by quant. data, which are as yet unavailable. The H model of Born and all models of He are rejected because they are paramagnetic, whereas the true mols. are diamagnetic. C. C. DAVIS

Atomic systems based on free electrons, positive and negative, and their stability. R. HARGREAVES. *Phil. Mag.* 44, 1065-1104(1922).—A theoretical and mathematical examn. of the stability relations in a system of positive and negative electrons, the fundamental arrangement of which is in 2 concentric circles, one contg. the negative electrons slightly within the other contg. the positive electrons. Both this scheme of arrangement and that of multiple positive core (Rutherford atom) are found to be essentially unstable, but discrimination is required as to the degree of instability, whether it exceeds the requirements for chem. reaction and free electrons. No attempt is made by H. to compare the mathematical results with actual expts. nor with other at. theories. S. C. L.

The path of an electron in the neighborhood of an atom. B. B. BAKER. *Phil. Mag.* 44, 777-86(1922).—A more generalized mathematical treatment of the mechanism proposed by Whittaker (*C. A.* 16, 3428) by which an electron imparts energy to an atom. The same conclusion is reached that an electron can permanently transfer energy to an hypothetical magnetic wheel within the atom, only if its velocity and direction are such that it penetrates the magnetic structure and passes out of its influence without returning on its path. S. C. LIND

Madagascar as a French source of radium. ADRIEN KARL. *Chimie et industrie* 8, 915-20(1922).—After a brief historical sketch of the development of the Ra industry, K. describes the Ra ores which occur in Madagascar and discusses the reasons for which they have not been appreciably worked so far. They consist largely of minerals of primary origin, while minerals worked at present (carnotite and autunite) are of secondary origin and easier to work up. Most Madagascar minerals (except *betafite*) contain Th, and the extd. Ra would contain meso-Th; but their U content (10-30%) is many times greater than that of the American ores. The reputed rarity of *betafite* is presumably due to the fact that no real search has been made for it. It can be worked by the same process as the American ores, is 8-10 times as rich in U, and contains only traces of Th. *Euxenite*, and similar minerals, are found in all the beryl deposits. The

presence of Th is not a drawback, as the greatest consumption of Ra at present is for radiferous preps. which are standardized a few hrs. before use and are rented according to their emanation content. The principle of the process for treating ores of primary origin on which K. is working at present is as follows: digest the pulverized mineral for 1 hr. at about 400° with H_2SO_4 under pressure in a rotary Fe autoclave. Pour the white pasty mass of sulfates into water, filter the ppt., which contains the radioactive elements with a very small amt. of rare earths and part of the rare-earth acids, and purify by successive treatments with Na_2CO_3 , HCl and H_2SO_4 followed by crystns. as chlorides and bromides.

A. P.-C.

The photographic action of Becquerel rays. KARL PRIZBRAM. *Sitzb. Akad. Wiss., Wien.* 130, 11a, 271-7(1921).—The observations of E. Mählestein (*C. A.* 15, 2382; also *Verh. d. Schweiz. Nat. Ges.* 101, 171-2(1921); *Arch. de Geneve* (5) 3, 294-5 (1921); *Phot. J.*, Aug. (1921)) concerning certain peculiar actions of α -particles on photographic plates are substantiated. Two new effects, "direct blackening" and "2nd negative," are observed. β and γ rays produce the same effects. Calcns. indicated that the same amt. of energy was absorbed by the plate for each type of radiation, in order to produce the different phenomena.

D. C. BARDWELL

The radioactivity of the springs in the region of Bagnoles de l'Orne, and its relation to geologic structure. P. LOISEL. *Compt. rend.* 175, 890-2(1922); cf. *C. A.* 16, 680.—A large no. of springs in a sector covering 100 sq. km. were analyzed for Ra Em. From the N. W. to the S. E. there is a general decrease in Ra Em content which follows the structural lines of the region. A few exceptions are noted.

D. C. BARDWELL

The ionium content of radium residues. ELISABETH RONA. *Ber.* 55B, 294-301 (1922).—The % sepn. of Io was detd. by adding known amts. of its isotope U X. Second residues from Ra extn. from Austrian pitchblende contained 16% of the Io found in the original pitchblende. Exhaustive extn. of pitchblende with HNO_3 gave a residue contg. practically no Io.

D. C. BARDWELL

The temperature ionization of elements of higher groups in the periodic classification. MEGH NAD SAHA. *Phil. Mag.* 44, 1128-39(1922).—S.'s theory of thermal ionization (*C. A.* 15, 468, 799, 1452, 2788, 3934, 3942), originally developed for single elements, has been extended by Milne (*The Observatory*, Sept., 1921) and by Russell (*C. A.* 16, 2635) to mixts. of elements. Certain discrepancies have appeared. For elements A and B with ionization potentials I_1 and I_2 , the Saha theory would require the ionization equilibria: $\log(K_1/K_2) = \log[x_1/(1-x_1)] - \log[x_2/(1-x_2)] = 5036 [(I_1-I_2)/T]$, where x_1 and x_2 are the fractions of A and B that are ionized at the abs. temp. T , I_1 and I_2 being expressed in volts. If $I_1 = I_2$, x_1 should equal x_2 . But for Na and Ba, I is 5.11 and 5.12 v., resp., while solar spectra of the sun-spots and of the sun itself show Ba to be completely ionized and Na much less completely ionized in both cases. In general the alk. earths under the same conditions are more highly ionized than the alkalis, which is illustrative of the general law that elements belonging to the higher groups of the periodic system are more easily ionized, and the successive steps of ionization follow each other in quick succession. Russell has suggested that consideration of the field of radiation would account for this, but S. proposes that it is a steric effect due to the double valence of Ba and hence a double chance for it to be ionized owing to its 2 valence electrons compared to 1 of Na, so that any force tending to remove one, will have twice the chance of striking or acting on one in the case of Ba, and so on for the higher groups. The reverse process of the elec. neutralization of Na or Ba by an electron may be considered sterically in the same way. On a Ca ion there would be a "negative patch" which would repel an electron, while on Na there is no such "patch." The steric factor is further considered statistically and thermodynamically and a formula is developed for the effective ionization: $I_e = I - 2.3 RT \log(n_e n_i)/23000$ volts, where

n_a and n_s are the resp. steric factors for the 2 ion species and are defined by the probability relation: $W = [(1/n_a) + (1/n_s)]^N$, where N is the total no. of particles of both species. Several elements are considered and their calcd. ionization is compared with the sidereal spectral results of Lockyer. S. C. LIND

Does an accelerated electron necessarily radiate energy? S. R. MILNER. *Phil. Mag.* 44, 1052(1922); cf. C. A. 15, 2241.—A note acknowledging the priority of Born (*Ann. Physik.* 30, 1(1909)) in recognizing that the accelerated electron does not according to the relativity principle radiate energy in the special case when moving with "Hyperbelbewegung" (motion of a particle whose world-line in 4 dimensions is hyperbolic). S. C. L.

The motion of electrons in argon and in hydrogen. J. S. TOWNSEND AND V. A. BAILEY. *Phil. Mag.* 44, 1033-52(1922).—Previous work (C. A. 16, 2070) showed such great differences between the motion of electrons in A and in H or N that it was desirable to repeat certain phases of the expt. using yet purer A. It is not only necessary to have A free from gases that will attach electrons to form negative ions, but also free from H and N, because the % of energy lost in an encounter with their mols., although small, is very large compared with that lost in an encounter with A mols. The method employed to purify A was to remove N by sparking in presence of O over caustic and then to remove the excess O by passing over a hot Cu foil. Both the elec. velocity and the velocity of agitation of the electrons were measured in pure H₂ in pure A, and in a mixt. contg. a small proportion of H₂ at different voltages and pressures. Large quantities of A produce but small effects on the velocity in H, but very small quantities of H produce large effects in A. The free path of an electron in A at 1 mm. pressure has a max. value of 1.6 cm. for a velocity of 3.75×10^7 cm./sec., corresponding to a potential fall of 0.39 v. In H at 1 mm. pressure the mean free path of an electron has a min. value 0.0195 cm. when the velocity is 7×10^7 cm./sec. As the velocity diminishes the path increases; when the velocity is 1.3×10^7 cm./sec. the path is 0.44 cm. The large increase of path with diminishing velocity is one of the most remarkable results of the investigation. S. C. LIND

Aging effect in the mobility of positive gas ions. H. B. WAHLIN. *Phys. Rev.* 20, 267-71(1922).—Mobilities of positive ions produced by α rays from Po were measured in dry air at pressures between 1 cm. and 3 cm. of Hg. With an auxiliary field of 1.5 v., the mobility is 1.35 cm. per sec.; with an auxiliary field of 3.0 v., the mobility is 1.80 cm. per sec. Higher voltages do not further increase the mobility. This indicates that the mobility of the ion decreases with age. The time required for aging is between $1/70$ and $1/110$ sec. This decrease of mobility could be due to the formation of a cluster ion. F. E. BROWN

Ultimate rays and spectral series. A. DE GRAMONT. *Compt. rend.* 175, 1025-9 (1922).—Following a brief exposition of the nature of the series which have been found for certain spectra, de G. points out that in every spectrum for which a principal series is known the first members of such series are the *raies ultimes* of the spectrum. Such rays are of extreme importance in spectrochem. analysis. For some elements, such as Ca, Zn and Cd, certain lines which represent inter-series combinations are also *raies ultimes*. If the relationship just pointed out holds for all elements, then a knowledge of the ultimate rays of the more complex spectra should be of value in establishing for them the series which as yet are unknown. Accompanying tables give the *raies ultimes* for spectra for which series are known. C. C. KIESS

Series regularities in the arc spectrum of chromium. C. C. KIESS AND HARRIET K. KIESS. *Science* 56, 666(1922).—At least 3 sets of series whose members are triplets occur in the arc spectrum of Cr. Of these, two sets are composed of wide triplets, and one set of narrow triplets. The wide-triplet series are parallel; i. e., there exist

const. differences between the wave nos. of homologous members. The characteristic triplet seps. are: $\Delta\nu = 112.44$, $\Delta\nu = 81.36$ and $\Delta\nu = 115.12$, $\Delta\nu = 91.45$ for the wide triplets of the 2 parallel series, and $\Delta\nu = 8.80$, $\Delta\nu = 5.65$ for the narrow-triplet series. Each component of the first member of the diffuse series is itself a narrow triplet.

C. C. KIESS

Spectrophotoelectrical sensitivity of argentite (Ag_2S). W. W. COBLENTZ. *Bur. Standards, Sci. Papers* No. 446, 265-80(1922).—The change in the elec. resistance of Ag_2S (argentite) when exposed to radiations from 0.3μ to 2μ was studied together with the effect of temp., the intensity of the radiation stimulus, and the mech. working of the material on the photoelec. sensitivity; and these results were compared with data obtained for Ag_2S (acanthite). Both forms react to wave lengths 0.5 to 1.1μ ; argentite shows a sharp sym. max. at 1.35μ while acanthite shows an unsym. max. at this wave length. The photoelec. sensitivity of each is increased at low temp. and the max. shifts hut to a different point for the two forms. The photoelec. reaction of argentite differs from acanthite in being free from an induced photonegative polarization. Hammering the crystals into thin sheets affects the sensitivity of each similarly. It is concluded that cryst. structure has a marked effect on spectrophotoelec. sensitivity.

HARRY B. WEISER

Relative intensities of the Stark effect components in the helium spectrum. J. S. FOSTER. *Phys. Rev.* 20, 214-20(1922).—A modified Lo Surdo tube was used. The axis of the tube was perpendicular to the slit. The sep. and parallel components were obtained by using the cross section of the cathode afflux where the field is a max. Pitting of the Al cathode caused a gradual shifting of the field. This caused blurring when exposures of several hrs. were made. With a 5-prism spectrograph, spectrograms were taken of the p and s components of the He lines $\lambda\lambda 4922$, 4472, and 4388 Å. in a field of 15000 v./cm. The energy distribution curves were calcd. from the contour of the images and the corresponding wedge densities, and the relative intensities were obtained by integration. The values for the main p components in order of increasing wave length are: for the line 4388, 8.2 (isolated), 4.1, 19.2, 28.0; for 4472, 168, 694; for 4922, 9.7, 31.6. Corresponding values for the s components are: for 4388, 1.0 (isolated), 3.0, 11.3, 9.5; for 4472, 76, 464; for 4922, 6.2, 21.4.

F. F. BROWN

Magnetic canal rays and the discharges from non-conducting particles. E. GOLDSTEIN. *Z. Physik* 11, 177-87(1922).—A qual. description of the luminous phenomena of nonconducting particles in the neighborhood of the anode of a discharge tube placed in a magnetic field.

C. C. KIESS

The band spectrum associated with helium. YUTAKA TAKAHASHI. *Proc. Phys. Math. Soc., Japan* 4, 187-93(1922).—The band spectrum of He consists of 2 double-headed bands, the lines of which form series for which Fowler has derived formulas of the Hicks type. Band spectra are usually attributed to mols. and not to atoms. Being an inert gas He exists normally only in the at. state. It is possible, however, to assume that under certain conditions unstable He mols. may exist from which the observed band spectrum may originate. A mathematical analysis shows that the form of a He mol. is such that 2 nuclei, each accompanied by one electron about it, are connected by means of an electron and form something like a nucleus, around which the remaining electron describes its orbit.

C. C. KIESS

Selective reflection of λ 2536 by mercury vapor. R. W. WOOD. *Phil. Mag.* 44, 1105-6(1922).

S. C. LIND

Polarized resonance radiation of mercury. R. W. WOOD. *Phil. Mag.* 44, 1107-11(1922).—The polarization of λ 2536 of a Hg arc was observed by passing the light through a system of quartz lenses and prisms, through a highly evacuated quartz vessel contg. Hg vapor at ordinary temp. and then through a quartz wedge, a double image

quartz prism into a camera with quartz lense. The presence of a few mm. of He, air, or H was found to suppress the polarization. Contrary to the experience with the polarization of I_2 vapor, H has a less effect than air on the polarization of Hg vapor.

S. C. LIND

The action of light on zinc sulfide. P. LENARD. *Ann. Physik* 68, 553(1922).—ZnS blackens rapidly when exposed to light from a Hg lamp. This is true of the ignited ZnS when pure and of the phosphorescent sulfides contg. impurities, but not of the unheated compd. The blackening is due to a film of finely divided Zn. It is destroyed by oxidizing agents, as O_2 , O_3 , H_2O_2 , and Cl while reducing agents, as SO_2 and CH_3O , promote it. The film is so thin that but a negligible trace of ZnO or $ZnCl_2$ is formed by repeated blackening and bleaching. The black surface film prevents the penetration of the light rays that cause the decompn. of the sulfide. The so-called "centers of phosphorescence" of the phosphorescent sulfides are not destroyed by repeated blackening and bleaching, which leads to the conclusion that the oxidizing agents which remove the blackening do not result in the formation of a new Zn compd. but in the reformation of the original mols. The oxidizing agent thus plays the role of a "catalyst." Blackening is not produced in the absence of an excess of H_2O vapor. HARRY B. WEISER

Theory of radiation-transformations. I. General mechanism of photochemical processes. F. WEIGERT. *Z. physik. Chem.* 102, 416-37(1922).—In the application of the Einstein law of photochem. equivalence, it has been assumed that the absorption of radiation takes place by quanta in single mols., as in the Bohr atom, the energy of the mols. being increased thereby. The passage of a single electron to an orbit of higher quanta has been assumed to be the first step of a true photochem. process. In order to remove some of the difficulties which result from this conception of photochem. transformations, it is now assumed that not a single mol., but a system of 2 mols. or mol. parts participates in the process of absorption. The distance between these 2 mols. can be bridged over by an electron in a photoelec. effect. In order that an absorbing system consisting of sepd. "electron-givers" and "electron-receivers" may be photochem. sensitive, the positive or negative mol. ions formed in the inner photoelec. effect need not be wholly stable, but there must be the possibility of a supplementary decompn. or another reaction. Since both an "electron-giver" and an "electron-receiver" are necessary for the formation of mol. ions, it is not correct, strictly, to speak of a photosensitive substance, but only of a photosensitive system. The fact that the sepn. of electrons is a primary process justifies the special importance of the "electron-giver" in photochem. reactions. This conception is related to that proposed by Winther: in photochem. oxidation-reduction processes the reducing agent is the real photosensitive component. In accordance with the principle put forward previously (cf. *C. A.* 16, 3810), the spacial distribution of the "electron-givers" is connected with the absorption spectrum and, therefore, also with the sensitiveness spectrum of the photochem. reaction. The significance of sensitiveness spectra and their variation under different conditions are discussed. The primary change of a photosensitive system (i. e., the origin of positive and negative mol. ions or the rearrangement of electrons in a single mol.) is the same, qualitatively, for all spectral regions in which the process occurs. This is effected according to the spacial sepn. of the electron "giver" and "receiver" through different energy quanta, $h\nu$. The closer the "giver" and "receiver" stand to one another, so much smaller is the no. of quanta necessary. These quanta may be less than the energy calcd. from the heat of reaction of the primary process of the elementary change. This representation has certain advantages over that hitherto employed, which requires that a single mol. in different regions of a wide absorption band takes up different amts. of energy, while the actual resultant chem. process is always the same. This hypothesis has led to the assumption of a division of the absorbed

energy into chem. and thermal. According to the new "dualistic" hypothesis, each constellation of "electron-givers" and "electron-receivers" absorbs during the process of absorption only the quantum (*Quant*) with which it is in tune, so that a partition of the energy quanta, which is in contradiction to the fundamental conception of the quantum theory, is not necessary. Whether the quantum of energy received from the "electron-giver" is employed chemically or thermally depends on whether the "electron-receiver" after its transition to a negative mol. ion is capable of further change or is stable. Since in all cases both kinds of "receivers" are present from the outset, and since those capable of change rapidly diminish, the yield of a photochem. reaction decreases with the duration of radiation.

H. JERMAIN CREIGHTON

Chemical luminescence and thermo-chemical behavior of organo-magnesium compounds. J. LIFSCHITZ AND O. F. KALBERER. *Z. physik. Chem.* 102, 393-415 (1922).—The chem. luminescence of organo-Mg compds. and their mol. compds. in reactions with a large no. of substances have been studied. Measurements have been made of the heat of reaction of a no. of luminescent and non-luminescent reactions, the results of which confirm those obtained by other investigators. These reactions include the formation of mol. compds. between a no. of organo-Mg halides and the solvent, Et_2O , the oxidation of several organo-Mg halides, the Wedekind-reaction, and the decompn. of aromatic and aliphatic Grignard compds. by H_2O . The abs. value of the heat of reaction does not exert a determinative influence on the appearance of luminescence, as has been assumed previously, while the differences of the heats of reaction do not afford an explanation of the luminescence-capacity of Grignard decompns. The relation between chem. luminescence and the formation of mol. compds. is discussed and an hypothesis of chem. luminescence is put forward. H. J. C.

Absorption colors of the second order (PICCARD) 25. Heinrich Rubens (WESTPHAL, *et al.*) 2.

CAMPBELL, N. R. *Modern Electrical Theory, Supplementary Chapters, Chapter XV; Series Spectra.* Cambridge University Press. 109 pp. 10s. 6d. Reviewed in *Chem. Weekblad* 19, 147(1922).

4—ELECTROCHEMISTRY

COLIN G. FINK

Electrochemical industry of Norway. OVE COLLETT. *J. four élec.* 31, 134-6 (1922).—Statistics are given for the electrolysis of alkali chloride solns., the production of Sn, Na, Al, CaC_2 , Fe-Si, Fe-Cr, Fe and steel, Zn, SiC and for H fixation.

C. C. VAN VOORHIS

The commercial and technical importance of aluminium. ANON. *Electrotechn. Z.* 43, 1457-8(1922).—German production in 1922 was 24,000 tons Al. A brief description of the process of manuf. is given. Then follows an account of the physical and chemical properties of the metal and its alloys. C. G. F.

The treatment of aluminium before nickel-plating. M. E. TASSILY. *Bull. soc. chim.* 31, 973-6(1922); cf. *C. A.* 8, 2529.—Further investigation showed that the use of Mn in the HCl bath possessed no advantage over that of Fe. Cf. Mazuir, *C. A.* 15, 989. H. M. McLAUGHLIN

Electroplating. R. CARL. *Oesterr. Chem.-Ztg.* 25, 9-11, 15-8(1922).—The conditions required for the deposition of Ni, Cu, Ag and brass are discussed. H. J. C.

Cells and batteries for weak currents and their theories. F. LEHNER. *Chem.-Ztg.* 46, 397-400(1922).—The processes which take place in a no. of simple cells are

discussed from the standpoint of the modern conception of the structure of the atom. It is shown that, theoretically, (a) 26.8 amp. hrs. are required for the dissoln. of one g. equiv. of metal; (b) the limiting e. m. f. is 3.8 v. for elements with aq. solns.; (c) if a g. equiv. is used at both electrodes the element should produce $3.8 \times 26.8 = 101.84$ watt-hrs.—a value never attained in practice.

H. JERMAIN CRIGHTON

The commercial applications of electroösmosis. J. H. FRYDLENDER. *Rev. prod. chim.* 25, 721-30(1922).—A review of the theoretical principles of electroösmosis and electrophoresis and of their application to drying peat, purifying and molding clay and kaolin, prepn. of colloidal SiO_2 , purification of tan liquors, tanning of hides, sterilizing and improving foodstuffs, preservation of green fodder, purification of glues and gelatins, prepn. of pure serums, extrn. of sugar from molasses, decolorizing sugar juices, purification and elimination of alkaloids, purification of crude glycerol, prepn. of $\text{Al}(\text{OH})_3$, and dehydration of coloring matters. The article is based very largely on the patent literature.

A. P.-C.

The production of carbon-black from natural gas by the high-voltage arc (JAKOWSKY) 21. Core oven loss (MAYER) 9. Manufacture of alloy steel for airplane shafts (KOTRINY) 9. Porcelain making and the electrical industry (ANON.) 19.

GRUBE, GEORG. *Grundzüge der Angewandten elektrochemie*. Vol. I. *Elektrochemie der Lösungen*. Dresden and Leipzig: Verlag von Theodor Steinkopff, 268 pp. Unbound 8s. 4d. Bound 10s. 3d. Reviewed in *Chem. News* 125, 318(1922); *J. Soc. Chem. Ind.* 47, 463R(1922).

Electric primary battery. L. W. WILLIS. U. S. 1,437,287, Nov. 23. Structural features.

Storage battery. R. L. WALSH. U. S. 1,436,616, Nov. 21. Structural features.

Storage battery solution. G. HOWARD. U. S. 1,437,343, Nov. 23. The soln. is formed from H_2SO_4 , H_2O , NaHCO_3 , Na borate and Na salicylate.

Tilting electric furnace. J. H. GRAY. U. S. 1,436,497, Nov. 21. The furnace is adapted for melting steel.

Rotatable mounting for lifting electric furnace roofs. H. F. PRIWER. U. S. 1,436,723, Nov. 23.

Electrolytic condenser. R. D. MERSHON. U. S. 1,437,189, Nov. 23. Structural features.

Apparatus for continuous strip electroplating. J. J. MUELLER. U. S. 1,437,003, Nov. 23.

Anode for electrolytic rectifiers. G. H. GROCE and G. M. HOWARD. U. S. 1,436,709, Nov. 23. An alloy of Pb 92 and Sb 8 parts is used for making rectifier anodes. The use of Sb renders the anode more durable.

Tungsten incandescent lamp filaments. F. S. GOUCHER. U. S. 1,436,717, Nov. 23. Wires for filaments are annealed, placed under strain by passage through a die and then passed through a zone of steep temp. gradient to render the wire "stable."

5—PHOTOGRAPHY

LOUIS DERR

The failure of the reciprocity law in photography. R. A. MALLEY. *Phil. Mag.* 44, 904-12(1922).—The failure of the blackening produced by light on a AgBr-gelatin plate to obey the reciprocity law was first studied quant. by Schwarzschild (*Astrophys. J.* 11, 89(1900)) who developed the formula: $S = KIT^p$, in which S is the blackening,

I the light intensity, T the time of exposure, and k and p consts. p , the so-called Schwarzschild const., has been studied by various investigators, but in all cases the blackening has been judged visually. M. has made a new exptl. study using 3 types of plate. The detn. of blackening was made definite by using an absorption wedge and measuring the length of line developed on the plate by an exposure of time T . The Schwarzschild equation was verified and it was shown that p is really const. under different conditions, but no phys. significance can yet be assigned to it. S. C. LINO

Colloid chemistry and photography. LIV. Acceleration of development and fogging by dyestuffs. H. LÜPPO-CRAMER. *Kolloid-Z.* 30, 114-7(1922). LV. Theory of acceleration of development by iodides. *Ibid* 186-7.—Many basic dyes accelerate the action of a quinol developer and no other; and, as physical development is similarly accelerated by acid dyes, the action is probably due to some colloid coagulation phenomenon. Methylene blue, which even in low concn. produces fog, considerably accelerates development with a slow non-alkaline metol-quinol developer. In the exposed areas the dye is decolorized before any Ag deposit appears. Fog is produced throughout the film by methylene blue and other dyes with neol (*p*-aminosalicylic acid) or catechol as developer, but only in the presence of salts of Mn, Cu, or Fe. The effects were studied by using a slow silvering bath as a system similar to a plate undergoing development; but the parallel is imperfect. In reply to criticisms of the author's "germ-exposure" theory, it is argued that the theory is not merely founded on certain development phenomena but explains the easy destruction of the Ag germs of synthetic photohalides and the visible or latent image by oxidizing agents when, and only when, they are treated with KI soln. L. DERR

Photographic methods of testing developers. J. I. CRABTREE. *Brit. J. Phot.* 69, 153-6, 170-2, 188-90(1922).—Tests should be carried out with the particular kind of emulsion for which the developer is intended. The film is exposed in strips, with exposure varied exponentially. In estimating developing power, time of appearance of image, rate of development after image appears, and power of developer to render min. exposure visible, are considered. In fog detn. the time required for appearance of fog is noted, and the total fog density after development is complete. The actual life of a developer is detd. by the time required for oxidation in the open air, and by the useful work with plates or papers before exhaustion. Color tests should be made in strips cut from a single sheet, to insure identity of emulsion. Other factors are the effects of dilution, temp., alkaliuity, cost, solubility, color, and crystalline form of ingredients. L. DERR

Retardation of development by dyestuffs. H. LÜPPO-CRAMER. *Die. Phot.* 1922, 29-30.—Dyes of the isocyanine group, especially ptaachrome, applied by bathing exposed plates, retard the action of certain developers and in some emulsions cause fog. The most susceptible developer thus far examined is neol. The fogging effect was prevented or reduced by increasing the concn. of the ptaachrome bath, or by preliminary treatment with 1:20,000 erythrosine soln. It is suggested that neol unites with the dye to form colloidal compds. which prevent crystallization of the Ag, and that the fogging and reversal phenomena observed are due to an unexplained secondary cause. L. DERR

Quantity of light energy required to render developable a grain of silver bromide. P. S. HELMICK. *J. Opt. Soc. Am.* 6, 998-1015(1922).—An ordinary AgBr photographic plate was exposed to a known amt. of nearly monochromatic light-energy, developed at const. temp., fixed and washed, and the number of reduced grains detd. by direct counting. A C-strip filament lamp supplied the light through a Hilger monochromatic illuminator, and the energy was measured by a linear thermopile. On the assumption that equal quantities of light give equal blackenings, the number of quanta per developed grain should be independent of the light-flux; and the results thus averaged give 2.3

quanta of incident light, of mean wave-length 540μ , as the amt. necessary to render a single grain developable.

L. DERR

Quantum theory of photographic exposure. II. I. SILBERSTEIN AND A. P. H. TRIVELLI. *Phil. Mag.* 44, 956-68(1922); cf. *C. A.* 16, 3441.—Recent work of Svedberg (*Phot. J.* Apr. 1922, p. 186) and of Svedberg and Andersson (*C. A.* 16, 391) are critically discussed and compared with the results reported in Part I. A further justification is given of the claim that if one grain in a clump is rendered developable the whole clump becomes so, which was contradicted by Svedberg. The additional evidence on this point appears to settle it very conclusively. The correction factor in the formula of the previous paper which had the result of reducing the effective area presented by the clump is then discussed. In the former paper it was interpreted as meaning that the light "dart" has a real finite cross-section, which must be wholly included in the clump area for its action to be effective. An alternate assumption is presented involving point incidence, the effect from which must spread over a certain area to be effective. Where the point incidence takes place so close to the edge that this spreading is prematurely cut off, the same formulation is arrived at as under the former assumption. Finally, an integral method is used to eliminate the error introduced by assuming a mean breadth for particles varying within a certain size-class. A cor. formula is deduced which is applied with better agreement to one set of data and which will be used in all future work.

S. C. LIND

Antistatic photographic film. A. F. SULZER. U. S. 1,432,366, Oct. 17. A cellulose ether film is used for backing photographic films mainly formed of a nitrocellulose compn. U. S. 1,432,367 relates to the similar use of a mixt. of cellulose acetate and cellulose ethyl ether.

Antistatic photographic film. A. F. SULZER. U. S. 1,432,368, Oct. 17. Nitrocellulose films coated with sensitive photographic compns. are rendered antistatic by combining a hygroscopic material such as glycerol with the nitrocellulose film and providing it with a backing layer of ethyl cellulose ether.

Antistatic photographic film. P. C. SEEL. U. S. 1,434,453, Nov. 7. Nitrocellulose photographic film material is rendered antistatic by an admixture of glycerol 2.5-5% and Na_2PO_4 0.5-1%. U. S. 1,434,454 specifies a film material of similar properties including sugar or other hygroscopic org. material and H_2O . The sugar, e. g., glucose, may constitute about 2-4% of the nitrocellulose compn. Cf. *C. A.* 16, 4152.

Photographic developer. W. DIETERLE. U. S. 1,432,542, Oct. 17. A developer is formed of "hydrochlorated *p*-amidosalicylic acid" or other sulfo-acid deriv. of an aminophenol, dissolved in caustic alkali soln.

Photographic process of preparing colored negatives. M. ULLMAN. U. S. 1,436,125, Nov. 21. Negatives are prepd. from originals adapted to reflect light from a portion of their surfaces by placing over the original a film of dichromated gelatin or similar material which becomes differentially sol. under the action of light without substantial change in its light-transmitting properties, transmitting light through the film to the original to be in part reflected, washing out the sol. portions of the film and dyeing the remaining portions.

Transfer photographic negative. M. ULLMAN. U. S. 1,436,629, Nov. 21. A transfer negative suitable for the production of printing plates is formed with an image of actinized dichromated gelatin or the like dyed to intercept all objectionably actinic light, e. g., by permethyl-*p*-rosaniline mordanted with "diaminostilbene-disulfoacid-dipiccol."

Printing plates. M. DE SPEERAT. U. S. 1,433,806, Oct. 31. Plates for printing with greasy ink are prepd. by exposing, developing and fixing a gelatin-Ag halide sensi-

tized layer, intensifying the image obtained, sensitizing the layer with a bath of alkali dichromate, exposing the layer to light from the back to render insol. the dichromated gelatin in the zones acted on by the light during the exposure, and washing the layer.

6—INORGANIC CHEMISTRY

II. I. SCHLESINGER

Systematic affinity principle. XVII. Parent- and mixed compounds in amines of lead halides. W. BULTZ AND W. FISCHER. *Z. anorg. allgem. Chem.* 124, 230-47 (1922); cf. *C. A.* 16, 4152.—The exptl. methods and app. were those used in preceding investigations. The following amines were found to be capable of existence; the temp. at which $p_{NH_3} = 100$ mm. follows each. Of $PbCl_2$: $8NH_3$, -36° ; $3.25NH_3$, -13° ; $2NH_3$, $+30^\circ$; $1.5NH_3$, $+34.6^\circ$; $1NH_3$, $+93^\circ$. Of $PbBr_2$: $8NH_3$, -38° ; $5.5NH_3$, -23° ; $3NH_3$, -9° ; $2NH_3$, $+42.5^\circ$; $1NH_3$, $+144^\circ$. Of PbI_2 : $8NH_3$, -51.5° ; $5NH_3$, -3° ; $2NH_3$, $+33^\circ$; $1NH_3$, $+88^\circ$; $0.5NH_3$, $+126^\circ$. Evidence is presented that some of these are mix-compds. formed from the parent compds. above and below them in the series: $4PbCl_2 \cdot 13NH_3 = PbCl_2 \cdot 8NH_3 + PbCl_2 \cdot 2NH_3 + 2PbCl_2 \cdot 3NH_3$, $2PbCl_2 \cdot 3NH_3 = PbCl_2 \cdot 2NH_3 + PbCl_2 \cdot 1NH_3$, $2PbBr_2 \cdot 11NH_3 = PbBr_2 \cdot 8NH_3 + PbBr_2 \cdot 3NH_3$, $2PbI_2 \cdot 10NH_3 = PbI_2 \cdot 8NH_3 + PbI_2 \cdot 2NH_3$, $2PbI_2 \cdot 1NH_3 = PbI_2 \cdot 1NH_3 + PbI_2$. XVIII. Amines of strontium halides. G. F. HURRIC. *Ibid* 322-32; cf. *C. A.* 16, 4153.—Exptl. methods and app. were those used in the earlier investigations. Stable compds. found (italicized ones are new), min. and max. p_{NH_3} measured, and Q values calcd. from the Nernst equation were as follows: $SrCl_2 \cdot 8NH_3$, 80 mm. at 0° , 610 mm. at 32.8° , 9.98 Cal. $SrCl_2 \cdot NH_3$, 63 mm. at 0° , 411 mm. at 108° , 19.5 Cal. at 0° , 12.5 Cal. at 78° , 13.4 Cal. at 108° . $SrBr_2 \cdot 8NH_3$, 9 mm. at 0° , 640 mm. at 63° , 10.9 Cal. $SrBr_2 \cdot 2NH_3$, 77 mm. at 63° , 276 mm. at 77° , 12.8 Cal. (also evidence for a labile isomer, 145 mm. at 63°). $SrBr_2 \cdot NH_3$, 115 mm. and 16.2 Cal. at 151° , 411 mm. and 17.3 Cal. at 215° . $SrI_2 \cdot 8NH_3$, 9 mm. at 0° , 550 mm. at 59.5° , 11.0 Cal. $SrI_2 \cdot 6NH_3$, 66 mm. at 63° , 438 mm. at 107.5° , 12.6 Cal. $SrI_2 \cdot 2NH_3$, 30 mm. at 107° , 196 mm. at 153° , 15.5 Cal. $SrI_2 \cdot NH_3$, 118 mm. at 208° , 251 mm. at 230° , 18.3 Cal. The temps. at which $p_{NH_3} = 100$ mm. are: $SrCl_2 \cdot 8NH_3$, 3.5° , $1NH_3$, 45.5° ; $SrBr_2 \cdot 8NH_3$, 30° , $2NH_3$, 63° , $1NH_3$, 146° ; $SrI_2 \cdot 8NH_3$, 31° , $6NH_3$, 74.5° , $2NH_3$, 134° , $1NH_3$, 204° . A. R. M.

Chemistry of the platinum metals. II. Alkali-ruthenium double sulfites. H. REMY. *Z. anorg. allgem. Chem.* 124, 248-74 (1922); cf. *C. A.* 15, 2596.—By treatment of warm K_2SO_3 soln. with a soln. of $RuCl_3$ and brief warming on a water bath a dark-violet ppt. was obtained of compn. $K_2SO_3 \cdot 2Ru(OH)SO_3 \cdot 3H_2O$. It is slightly sol. in water, sol. in dil. acids to a dark-violet soln. without evolution of SO_2 ; from this soln. $BaCl_2$ gives no ppt. in the cold and a violet ppt. on warming. Readily sol. in dil. NH_3 soln. with intense indigo-blue color. The salt is clearly complex and a probable structural formulation is given. From the mother liquor of the preceding salt after long vigorous boiling a small ppt., dark-gray, was obtained. Owing to the minute amt. analysis was not very certain and the compn., $K_2SO_3 \cdot 3RuSO_3 \cdot 6H_2O$, is preliminary. To a warm soln. of 20 g. Na_2SO_3 in 500 cc. water 30 cc. of a soln. of RuO_4 , treated 2 hrs. previously with concd. HCl , was added and the mixt. heated to boiling. A microcryst. bright-green-blue ppt. resulted of compn. $7Na_2SO_3 \cdot 2RuSO_3 \cdot 7H_2O$. In a repetition which differed only in that the Na_2SO_3 soln. was boiling during addn. of the Ru soln., a salt of the same tint pptd. but redissolved and was obtained upon addn. of Na_2SO_3 crystals as a pale-green-blue ppt. Analysis indicated $7Na_2SO_3 \cdot 2RuSO_3 \cdot 9H_2O$. The 2 salts differed distinctly in many reactions. Strong acids cause evolution of SO_2 upon warming but even long boiling removes it incompletely. Two K, and a Na, complex sulfites of blue color were obtained which were believed to be contaminated

with alk. sulfite. The residues from all three after removal of alk. sulfite and water showed the compn. RuSO_4 . Analysis of these compds. is very difficult particularly for sulfite. For this no known method is adequate. Analytical procedures are discussed with much detail and a highly ingenious graphical method by which errors in the sulfite detns. were evaluated is given in full but is not suitable for abstracting.

A. R. M.

Isomerism of metallic oxides. I. Lead monoxide. M. P. APPLEBEY AND R. D. REID. *J. Chem. Soc.* 121, 2129-36(1922).—This paper controverts the recent theory of Glasstone (*C. A.* 16, 368, 1955) that apparent differences of properties are due to states of division. PbO was prepd. in well crystd. forms by dehydration of pure $\text{Pb}(\text{OH})_2$ in strong KOH solns. at nearly boiling temp. The form obtained depends on concn. of alkali and rate of cooling, rapid cooling favoring the yellow form. The following forms were obtained: KOH 15 *N*, red, square plates, tetragonal, uniaxial, negative to polarized light; KOH 10 *N*, yellow, rhombic bipyramidal needles, biaxial, positive to polarized light; KOH 3 *N*, steel-black, like the yellow form in optical properties. This confirms Nordenskiöld (*Pogg. Ann.* 114, 619(1861)) and Larsen (*C. A.* 16, 541). Peroxide content, yellow 0.67%, red 0.63%. The black form has not yet been investigated in detail but some observations indicate that it is formed when the yellow needles are exposed to light either in vacuum or in air. Densities, red 9.27, yellow 8.70. The solubilities of the 2 forms in *N* NaOH were measured gravimetrically and electrometrically. At 20° the soly. of the yellow form is about 1.8 that of the red form. The evidence from soly. and examn. of cryst. form shows the yellow and red forms to be polymorphic modifications. The electrode $\text{Hg}|\text{HgO}$ in *N* NaOH was found to be easily reproduced and const. over long periods. The following consts. were found at 20°. Column 3 contains Glasstone's results for what he regarded as the single oxide. As his data approximate those for the more sol. yellow form, the authors conclude that a mixt. of the 2 forms was present in his material.

	Red form.	Yellow form.	G.'s form.
E. m. f., $\text{Pb} \text{PbO}$ in <i>N</i> NaOH , volts	0.5668	0.5594	0.562
Pb^{++} concn. in <i>N</i> NaOH , gram-ion per l.	0.90×10^{-15}	1.80×10^{-15}	1.6×10^{-15}
$[\text{Pb}^{++}][\text{OH}^-]^2$	0.47×10^{-19}	0.91×10^{-19}	0.82×10^{-19}
Acid dissoc. const., $\text{Pb}(\text{OH})_2$	0.33×10^{-11}	0.39×10^{-11}	1.3×10^{-12}

A. R. MIDDLETON

Subordinate valence of the hydroxyl group. II. Complex salts of nuclear-substituted pyrocatechol derivatives. HANS REHLEN AND ADOLPH SAPPER. *Z. anorg. allgem. Chem.* 124, 275-88(1922); cf. *C. A.* 16, 4154.—The problem here investigated was to show, by synthesis of compds., whether a diaquo-diacido complex of a dibasic acid or a 1,2-dihydroxybenzene deriv. has a coordination no. 4 or 6. Replacement of nuclear H in a diaquodipyrocatechol complex by a substituent like carbonyl which can exert a strong secondary valence should result in formation of polynuclear compds. in which one or both aquo groups of one mol. are replaced by carbonyl of the other mol. The octahedral formula would require formation of bridge compds. with 3 aquo mols. to 2 nuclear metal atoms while the tetrahedral formula would require only 2 aquo mols. Three such compds. were prepd. In certain cases 5- and 6-nuclear compds. resulted for which a satisfactory explanation on the tetrahedral basis was found. Instead of pyrocatechol, protocatechualdehyde (3,4-dihydroxybenzaldehyde) was used and 3 metals were employed in addn. to those of the first investigation. In contrast to the compds. of pyrocatechol, these compds. are not decompd. by air and crystallize readily. The following new compds. are described. ($P = \text{C}_6\text{H}_4\text{O}_2$) *Na diaquo-protocatechualdehydodisulphate*, $\text{Na}_4[\text{Cu}_2\text{P}_2(\text{H}_2\text{O})_2] \cdot 7\text{H}_2\text{O}$, by mixing warm solns. of 7.5 g. CuSO_4 in 12 cc. water and 10.4 g. aldehyde in 45 cc. 4 *N* NaOH . After a day fine green-yellow prisms,

which, recrystd. from hot water contg. bone-black, form brighter olive-green crystals. Yield, 11.5 g. $\text{Na}_4[\text{Zn}_2\text{P}_4(\text{H}_2\text{O})_2] \cdot 18\text{H}_2\text{O}$ from hot solns. of 8.64 g. ZnSO_4 in 15 g. water, 10.35 g. aldehyde in 25 cc. water and then 21 cc. 10 *N* NaOH; evapn. in desiccator gave 14 g. crude; recrystn. from 35 g. water, 10 g. brilliant, pale-yellow crystals. $\text{Na}_4[\text{Ni}_2\text{P}_2(\text{H}_2\text{O})_2] \cdot 18\text{H}_2\text{O}$ from 1.5 g. protocatechuic acid in 20 cc. 2 *N* NaOH and 5 cc. 2 *N* NiCl_2 ; a slimy ppt. soon vanishes nearly completely; soln. filtered after 24 hrs. and equal vol. EtOH added; bright-green needles, 0.8 g. *Na diaquo-tetra-protocatechuic-ethyl ester-dinickelate*, $\text{Na}_4[(\text{H}_2\text{O})_2\text{Ni}_2(\text{OC}_6\text{H}_4\text{O} \cdot \text{CO}_2\text{C}_2\text{H}_5)_4] \cdot 25\text{H}_2\text{O}$, from 6.1 g. ethyl-protocatechuate in 27 cc. 4 *N* NaOH and a warm soln. of 3.6 g. $\text{Ni}(\text{AcO})_2$ in 17 cc. water; bright-green scales, effloresce readily. Also the following compds. with 5 or 6 nuclear metal atoms: $\text{Na}_{11}[\text{Ni}_2\text{P}_{10}(\text{C}_7\text{H}_4\text{O}_2 \cdot \text{OH})\text{H}_2\text{O}] \cdot 45\text{H}_2\text{O}$; $\text{Na}_{12}[\text{Ni}_3\text{P}_{10}(\text{C}_7\text{H}_4\text{O}_2 \cdot \text{OH})(\text{OH})(\text{H}_2\text{O})_4] \cdot 50\text{H}_2\text{O}$; $\text{Na}_{13}[\text{Cd}_3\text{P}_{10}(\text{C}_7\text{H}_4\text{O}_2 \cdot \text{OH})] \cdot 54\text{H}_2\text{O}$. For details of prep. of these salts the original must be consulted.

A. R. MIDDLETON

Preparation and reactions of stannous oxide and stannous hydroxides. F. W. BURY AND J. R. PARTINGTON. *J. Chem. Soc.* 121, 1998-2004(1922).—To check discrepant statements in the literature, samples were prepd. by methods used by previous investigators and analyzed. Conclusions: Six samples prepd. by various methods were essentially the same; none could be obtained quite Cl-free although the amt. was negligible in most cases. The analytical data agree most closely with Ditté's (*Ann. chim. phys.* [v], 27, 145(1882)) formula $3\text{SnO} \cdot 2\text{H}_2\text{O}$. Little or no reaction occurs at room temp. between moist hydrated and oxide air. Under water it slowly loses water and changes to SnO . It is stable at 110° but does not lose all its water at 160° . The ppt. from SnCl_2 soln. by NH_3 appears to be the usual hydrated oxide and not a basic salt. Many reactions given in the literature could not be verified.

A. R. M.

Inorganic complex salts, crystallographic and optical study. I. ISABEL E. KNAGGS. *J. Chem. Soc.* 121, 2009-79(1922).—The following salts were studied: (1) $\text{K}_4[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$; (2) $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$; (3) $\text{NH}_4[(\text{NH}_3)_2\text{Co}(\text{NO}_2)_2\text{C}_2\text{O}_4] \cdot \text{H}_2\text{O}(\text{cis})$; (4) the *trans* form of the same; (5) *cis*- and (6) *trans*- $\text{K}[(\text{NH}_3)_2\text{Co}(\text{NO}_2)_2\text{C}_2\text{O}_4] \cdot \text{H}_2\text{O}$; (7) $\text{Ba}[(\text{NH}_3)_2\text{Co}(\text{NO}_2)_2\text{C}_2\text{O}_4] \cdot \text{H}_2\text{O}$; (8) $\text{NH}_4[(\text{NH}_3)_2\text{Co}(\text{NO}_2)_2]$. Only racemic compds. were examd. (1) and (2) are holohedral monoclinic and isomorphous. (3), (5) and (7) show close isomorphism and belong to the ditrigonal-scalenohedral class of the rhombohedral system. (4) and (6) are holohedral monoclinic but not truly isomorphous. (8) is holohedral orthorhombic. Full details of the optical examn. are given.

A. R. M.

Purification and analysis of zirconium dioxide. F. G. JACKSON AND L. I. SHAW. *J. Am. Chem. Soc.* 44, 2712-14(1922).—Fusion for 1 hr. of 1 pt. oxide to 4 pts. of an equal mixt. of borax and soda ash dissolved 60-70%. When the fusion is taken up in dil. HCl the insol. residue cannot be sepd. by filtration. By pptg. the hydroxide with NH_3 the residue was held in this ppt. which could be washed free of borates and chlorides. By repeatedly pouring a slight excess of warm HCl over the ppt. the hydroxide can then be dissolved and the soln. filtered clear. Addn. of a very little H_2SO_4 then pptd. the basic sulfate which could be coagulated by heating nearly to boiling and washed free from Fe and Al. Most of the Ti is pptd. Attempts to det. Zr by volatilization of the fluoride in absence of H_2SO_4 were not successful. Twelve successive treatments with H_2F_2 reduced the residue to 2%.

A. R. M.

Absorption of carbon disulfide vapor by solutions of sodium trinitride. A. J. CURRIER AND A. W. BROWNE. *J. Am. Chem. Soc.* 44, 2849-54(1922).—A 1% soln. was found to absorb irreversibly about 3.5 times its vol. of CS_2 vapor with quant. formation of Na azido-dithiocarbonate, NaSCSN_3 . With 5% or satd. aq. solns. satisfactory absorption was obtained of CS_2 vapor in mixts. with air, O_2 , N_2 , H_2 , CH_4 and CO. Repeated contacts for 1 min. with intermediate withdrawals from the pipet gave better results than prolonged contact. The soln. of azido salt formed in the reaction

was found to possess no dangerously explosive properties but to decomp. very slowly after long standing with formation of N_2 , S and NaSCN. A. R. M.

Germanium. IV. Germanium tetraiodide. L. M. DENNIS AND F. E. HANCK. *J. Am. Chem. Soc.* **44**, 2854-60(1922); cf. *C. A.* **16**, 1189.—The method of prepn. consisted of heating powd. Ge in I_2 vapor carried by a current of CO_2 . Reaction began at 212° and was very rapid at 360° . In the prepn. GeI_4 light-yellow crystals, was also isolated. GeI_4 m. 144° ; $d_4^{25} = 4.3215$ in concd. H_2SO_4 ; forms regular octahedrons; color in lump form varies with temp. from canary-yellow at -185° to ruby-red at $+144^\circ$. At room temp. it is coral-color in lump form and orange in powder. It dissociates at 440° , into GeI_2 and I_2 . Contrary to Winkler GeI_4 neither gained nor lost wt. when exposed to air 2 days and 0.56 g. lost but 6.5 mg. in 5 mos. It is decompd. by little water to GeO_2 , not affected appreciably by cold concd. H_2SO_4 , is dissolved by 1:4 KOH and slowly by concd. HCl; it is decompd. at once by concd. NH_3 soln. Its behavior with 23 org. liquids is described in all of which it dissolves. In some of these the soln. underwent no apparent change in 4 mos., in other slow decompn. and in still others immediate decompn. took place. A. R. MIDDLETON

Properties of ammonium nitrate. IV. The reciprocal salt-pair, ammonium nitrate and sodium chloride. E. P. PERMAN. *J. Chem. Soc.* **121**, 2478-83(1922); cf. *C. A.* **16**, 3248.—Cooling curves and the equil. diagram are given for the system, $NH_4NO_3 + NaCl \rightleftharpoons NaNO_3 + NH_4Cl$. The diagram shows ternary pts. at 133° for $NaCl$, $NaNO_3$ and NH_4Cl and at 112° for NH_4NO_3 , $NaNO_3$ and NH_4Cl . No isomorphous mixts. or double salts are formed. The f. p. of NH_4NO_3 is lowered from 169° (a) to 141° by addn. of NH_4Cl ; (b) to 121° by addn. of $NaNO_3$; (c) to 112° by addn. of $NaNO_3$ and NH_4Cl . Details as to f. ps. of the various binary and ternary mixts. are collected in an appendix. A. R. M.

Alleged variable composition of triple chlorides containing silver and gold. H. L. WELLS. *Am. J. Sci.* **4**, 476-83(1922).—W. admits the claim of priority by Emich and his associates but combats their contention of variable compn. By calcs. based on analyses of Bayer (*C. A.* **14**, 3605) it is shown that B.'s material was contaminated with $Cs_3Au_2Cl_{14}$ and $CsAuCl_4$. From analogy it is concluded that the triple bromides analyzed by Suschnig (*C. A.* **16**, 2816) were also mixts. Bayer's own analyses are shown to indicate that the Rb salt is a definite compd. with compn. $Rb_3Ag_2Au_3Cl_{17}$, corresponding to the formula found by W. for Pollard's salt. A. R. M.

Boron hydrides. M. L. HUGGINS. *J. Phys. Chem.* **26**, 833-5(1922).—Structures are proposed for B_7H_8 , B_8H_{10} , B_9H_{12} and $B_{10}H_{14}$ analogous to those of ethylene, butadiene, benzene and naphthalene, resp. These are based on the idea that B has but 3 valence electrons and that the residual affinity of the B=B bond is sufficient to hold H atoms although incapable of holding larger atomic kernels. The H atoms are held by 4-electron bonds, such as may exist (temporarily at least) in unsatd. C compds, each bond being surrounded by 4 atoms. A. R. M.

Cuprammonium sulfate. G. N. RIDLEY. *Chem. News* **125**, 288(1922).—No new matter. A. R. M.

Hydrates of sodium sulfide. A. SANFOURCHE AND MILE. A. M. LIEBAUT. *Bull. soc. chim.* **31**, 966-72(1922).—The usual methods of thermic analysis were employed using freshly recrystd. $Na_2S \cdot 9H_2O$. For the higher concns. this was dehydrated by heating rapidly which caused formation of 0.2-0.3% thiosulfate and traces of sulfate. Analysis was by titration with ammoniacal $AgNO_3$ which reacts only with sulfide. Difficulties were encountered in the extreme tendency to superfusion and low thermic cond. The irregular and marked lags of the cooling curves were corrected by reheating. The rounding of angular points, particularly in mixts. rich in Na_2S , was overcome by recourse to Stock's (*C. A.* **3**, 2527) sintering-point method. Of the various hydrates

claimed by previous investigators only two could be confirmed, those with 9 and 5.5 mols. water. Evidence was obtained for the existence of a new hydrate, $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$, but less certain than that for the others owing to exptl. difficulties in its field. The hydrates with 5.5 and $1\text{H}_2\text{O}$ appear to undergo a transformation to the solid state.

A. R. M.

Preparation of sodium bismuth thiosulfate and its use in the determination of potassium. V. CUTSINIER. *Bull. soc. chim.* 31, 1064-8(1922).—The following method gave the double salt in well crystd. form. 10 g. BiONO_2 is dissolved in 10 cc. HCl with heat, the soln. cooled and made up to 100 cc. with 95% EtOH and sufficient HCl to keep the soln. clear. To this is added an aq. soln. of 20 g. Na thiosulfate crystals in a vol. of 100 cc. and then 1000 cc. of 95% EtOH is added gradually and, if necessary, HCl drop by drop to maintain perfect clarity. After about 15 min. a canary-yellow cryst. ppt. deposits, which is not altered by contact with the mother liquor for 24 hrs. The ppt. is filtered, washed with EtOH , at first acidified with HCl , then pure, and dried to const. wt. over H_2SO_4 in vacuum. Analysis agreed but fairly with $\text{Na}_2\text{Bi}(\text{S}_2\text{O}_3)_3$ but the salt browns rapidly in air. The salt dissolves easily and without residue in water but the soln. is acid. It does not give the reaction for thiosulfate with ferric salts until very nearly neutralized with Na_2CO_3 . EtOH 95% ppts. it from the aq. soln. even if acidified. From this method of prepn. it is to be expected that the salt would also ppt. in the detn. of K by Carnot's method. Data are given showing this to be the case. K found is always too high and varies with the amt. of reagent used and also with the amt. of EtOH added. Detns. under precisely similar conditions give varying results. The reagent is not applicable to the detn. of K.

A. R. MIDDLETON

Constitution of the Erdmann salt and its derivatives. E. H. RIESERFELD AND R. KLEMENT. *Z. anorg. allgem. Chem.* 124, 1-21(1922).—Ixp'tl. proof is set forth that the NH_2 groups occupy *trans* positions in Erdmann's salt, $\text{NH}_4[(\text{NO}_2)_2\text{Co}(\text{NH}_3)_2]$, and its dioxalato, oxalato and dichloro derivs. *Cis*-positions of these groups should make possible (1) optical isomers, (2) replacement of the 2 NH_2 groups by a mol. of ethylenediamine without essential alteration of the complex. Both NH_4 and K Erdmann's salt gave $[(\text{NO}_2)_2\text{Co} \text{ en } \text{NH}_2]$. By treatment with HCl at 0° Erdmann's salt was transformed into green, *trans*- $[\text{Cl}_2(\text{H}_2\text{O})_2\text{Co}(\text{NH}_3)_2]\text{Cl}$. A new, much simpler method is described for prepn. of $\text{NH}_4[(\text{C}_2\text{O}_4)_2\text{Co}(\text{NH}_3)_2] \cdot \text{H}_2\text{O}$ from the dichlorodiaoquo chloride and $\text{H}_2\text{C}_2\text{O}_4$ and pptn. by EtOH satd. with NH_4Cl . No optical isomers could be obtained by fractional crystn. of its strychnine salts; it yielded $[\text{C}_2\text{O}_4)_2\text{Co} \text{ en } (\text{NH}_3)_2] \cdot 0.5\text{H}_2\text{O}$. Fractional crystn. of the strychnine salts of $\text{NH}_4[(\text{NO}_2)_2\text{Co}(\text{C}_2\text{O}_4)_2\text{Co}(\text{NH}_3)_2] \cdot \text{H}_2\text{O}$ yielded no optical isomers; it was transformed into green $[\text{Cl}_2(\text{H}_2\text{O})_2\text{Co}(\text{NH}_3)_2]\text{Cl}$ and this into the purple-violet dioxalato salt; with ethylenediamine decompn. of the complex took place with formation of brown-red $[(\text{CH}_3)_2\text{N}(\text{NH}_3)_2][(\text{NO}_2)_2\text{C}_2\text{O}_4\text{Co}(\text{NH}_3)_2] \cdot 2\text{H}_2\text{O}$. The ready prepn. of $\text{R}[(\text{NO}_2)_2\text{Cl}_2\text{Co}(\text{NH}_3)_2]$ from Erdmann's salt is, with consideration of the above, sufficient proof of its structure. Attempts to substitute malonato for oxalato groups were unsuccessful because of the great soly. of these salts and easy reducibility of malonic acid. A new ammonium cobaltomalonato, $(\text{NH}_4)_2\text{Co}(\text{C}_3\text{H}_3\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$, was obtained. It forms bright-rose crystals, very sol. in water.

A. R. M.

Composition of Scheele's Green. G. BORNEMANN. *Z. anorg. allgem. Chem.* 124, 36-8(1922).—Some analytical data are submitted from which the following conclusions are drawn: (1) as prepd. by Scheele's method the compn. approximates that of a neutral arsenite, $3\text{CuO} \cdot \text{As}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ rather than CuHAsO_3 ; (2) the compn. varies with method and materials of prepn. and is richer in CuO in proportion to the excess of caustic alkali or carbonate employed.

A. R. M.

Formation of oxides of polyvalent metals from their hydroxides. I. HANS EULER

AND ULF VON EULER. *Z. anorg. allgem. Chem.* **124**, 70-80(1922).—This transformation has been shown to exhibit considerable analogy to the dehydration which accompanies and probably conditions coagulation of albumins. The remarkably great temp. coeff. is characteristic of the latter, the reaction velocity being doubled by a temp. increase of 2°. Whether the dehydration of metallic hydroxides shows a temp. coeff. of similar large value was here investigated in the case of $\text{Cu}(\text{OH})_2$. The material was prepd. (1) by mixing equiv. amts. of CuSO_4 and NaOH in N soln. at 15° and centrifuging till SO_4 -free; (2) by electrolysis with Cu electrodes in 0.5 N KNO_3 at 0.02 amp. per cm^2 and dialyzing till NO_3 -free. Both preps. showed $p_H=8-9$. The times were observed in which 25% of the $\text{Cu}(\text{OH})_2$ was changed to CuO at various temps. The temp. coeff. per 5° found was 3.0, 40-45°; 2.6, 45-50°; 2.0, 50-55°; 1.8, 55-60°. This is of the same order as that of the coagulation of egg albumin. A. R. M.

The constitution of the aluminates. JAROSLAV HEYROVSKY. *Chem. News* **125**, 198-200(1922).—From the slight changes in the lowering of the f. p. and the regular fall of cond. observed in solns. of alkalis and alk. earths, gradually satd. with nascent $\text{Al}(\text{OH})_3$ H. concludes that in solns. more dil. than 0.1 N only monovalent aluminate ions exist. In contact with cryst. $\text{Al}(\text{OH})_3$ such solns. are 50% hydrolyzed, though with nascent $\text{Al}(\text{OH})_3$ only 1-1.5%. H. agrees with Pfeiffer (*C. A.* **2**, 501) that the soln. of $\text{Al}(\text{OH})_3$ in alkalis is by the formation of a complex anion and not by neutralization. Since 4 and 6 are the coordination numbers of Al , its complex anions are of the type AlX_4 and AlX_6 . Experimentally in dil. solns. only $\text{Al}(\text{OH})_4^-$ ions were detected.

M. O. LAMAR

Hydrates of carbon, so-called. B. L. VANZETTI. *Atti. realei st. Veneto* **79**, 471-86 (1920).—Ground spiegeleisen was treated with CuSO_4 , the pptd. cure dissolved with acidified FeCl_3 , and the product dried at 100°. 100 g. of the metal give 7 g. of brownish-black, deuse mass. The water still held is driven off at 250°. It burns readily in air. Heating in a closed tube at 150°, does not change the wt.; but at 200° the loss is 6.5%, and at 235°, it is 18.1°; the loss is due to H_2 , O_2 , CO . At higher temp. the loss is greater, but the residue is never pure carbon. In a current of H_2 all the O_2 is eliminated, but 3% H_2 is retained, which, with the halogens, easily gives halogenated products. This is a case of *adsorption*; water is held by the amorphous carbon as H_2 is held by Pd .

A. W. CONTIERI

Silver ammonia fluoride. DERVIN AND OLMER. *Compt. rend.* **175**, 1058-61 (1922).—Crystals of silver ammonia fluoride are prepd. by the slow evapn. under vacuum, of a soln. of AgF in concd. NH_4OH . The crystals are hygroscopic and very sol. in water. The compn. corresponds to the formula $\text{AgF} \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$. Above 100° the compd. is readily detonated. J. A. ALMQUIST

BRÜCK, ERNST AND WEISSENBERGER. G. Kurzes Repetitorium der Chemie zum Gebrauche für Mediziner, Pharmazeuten, Lehramtskandidaten, Chemiker, Landwirte u. a. m. Nach den Werken und Vorlesungen von Arnold Bernthsen, Erdmann, Holleman, Hofmann, Kraft, Ostwald, Pinner, Remsen, Richter, Smith, Schmidt u. a. I. Anorganische Chemie. 6th revized ed. Leipzig: J. Ambrosius Barth.

DENHAM, H. G. An Inorganic Chemistry. London: Edward Arnold & Co. 683 pp. 12s. 6d. Reviewed in *Chem. News* **125**, 44; and *Chem. Age* (London) **7**, 168 (1922).

HOLMYARD, R. J. Inorganic Chemistry. London: Edward Arnold & Co. 560 pp. 6s. 6d. Reviewed in *Chem. Age* (London) **7**, 672(1922).

KLEIN, J. Chemie Anorganischer Teil. 7th ed. Revized. Berlin: Sammlung Goschcn. M12.

NORRIS, JAMES F. and MARK, KENNETH L. Laboratory Exercises in Inorganic

Chemistry. New York: McGraw-Hill Book Co. 548 pp. \$2.00. Reviewed in *Chem. Bull.* (Chicago) 9, 258(1922).

7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

Colloid chemistry and analytical chemistry. W. BÜTTGER. *Kolloid-Z.* 31, 256-8 (1922).—A lecture to colloid chemists showing how the study of colloids has helped the analyst. W. T. H.

The constancy of the permanganate titer and different methods of obtaining the titer. O. HACKL. *Chem.-Ztg.* 46, 1065(1922).—Further evidence is produced in support of the fact that a pure KMnO_4 soln. will keep indefinitely and that $\text{Na}_2\text{C}_2\text{O}_4$ is the most satisfactory substance to use in standardization. W. T. H.

The "excess" of reagents in chemical analysis. J. GROSSER. *Chem.-Ztg.* 46, 1059-60(1922).—A plea, largely in the interest of economy, for greater definiteness in prescribing the quantities of reagents to be used in quant. analysis. W. T. H.

Reductions with cadmium and lead in volumetric analysis. III. W. D. TREADWELL. *Helvetica Chim. Acta* 5, 806-18(1922); cf. *C. A.* 17, 39.—1. *Titration of alkali chlorate and perchlorate.*—If a hot soln. of alkali chlorate in dil. H_2SO_4 is passed through a Cd reductor, the chlorate is reduced quantitatively to chloride which can be titrated with Ag thiocyanate by the method of Volhard. If a mixt. of chlorate and perchlorate is given this treatment, only the former undergoes reduction. If, however, the soln. contains a little Ti^{+++} the perchlorate is reduced. After the reduction, the Ti^{+++} may be oxidized very carefully with KMnO_4 and the chloride detd. by the Volhard method or by electrometric titration with Ag^+ . 2. *Titration of columbium.*—A no. of expts. were performed in the hope of finding conditions such that the Cb would be reduced quantitatively to the tervalent condition but it was found difficult to get a stable, highly dispersed system contg. Cb at sufficient concns. The conditions recommended by Osborne (*Am. J. Sci.* [3] 30, 329) could not be greatly improved and objection is raised to the use of solns. of such great acidity. 3. *Titration of molybdenum.*—By dipping Zn rods in $\text{Pb}(\text{AcO})_2$ soln. a deposit of Pb was obtained which could be scraped off and used in a reductor. With a 3-8 cm. layer of such Pb it was found possible to reduce MoO_4^{--} quantitatively to Mo^{+++} . The soln. of reduced Mo was caught in a flask filled with CO_2 and the HCl soln. titrated with KMnO_4 in the presence of excess MnSO_4 . 4. *Titration of stannic ions.*—Similarly, by passing a strongly acid soln. of SnCl_6^{--} through a Pb reductor, a soln. of Sn^{++} was obtained which could be titrated with KMnO_4 in the presence of MnSO_4 . W. T. H.

Electrometric acidimetry and alkalimetry without the use of hydrogen. P. A. VAN DER MEULEN and F. WILCOXON. *Ind. Eng. Chem.* 15, 62-3(1923).—If a polished Pt wire is immersed in the aq. soln. of an acid, with a calomel half cell as the other electrode, a fairly stable potential is obtained and its value changes as the acid is neutralized. The rate of change reaches a max. when the soln. is at the neutral point. In the usual titrations with the H_2 electrode, the Hg of the half cell is the positive electrode but in these titrations the Hg was negative except when the soln. was quite far on the alkaline side of the neutral point. If a beaker of HCl soln. contained electrodes consisting of a Pt plate and a graphite rod, an e.m.f. was established such that the acid could be titrated without the use of the half cell. W. T. H.

Some applications of oxygen electrode, air electrode, and oxidation potential measurements to acidimetry and alkalimetry. N. H. FURMAN. *J. Am. Chem. Soc.* 44, 2685-97(1922).—Acids and bases can be detd. in the presence of highly colored, strong oxidizing agents by an electrometric titration. The O_2 electrode, an air electrode or a

platinized electrode gives accurate results in the titration of total alkalinity or acidity and the results are, in general, analogous to those obtained with the H_2 electrode. As colored oxidizing agent, a chromate or dichromate was used. W. T. H.

The use of malic, maleic and fumaric acids in volumetric analysis. N. A. LANGE AND H. KLINE. *J. Am. Chem. Soc.* **44**, 2709-12(1922).—Either of these acids may be used for standardizing NaOH solns., giving values fully as accurate as obtained in standardizing HCl solns. by weighing AgCl. Malic and fumaric acids may be used for standardizing $KMnO_4$ solns. but they have no advantages over $Na_2C_2O_4$. Succinic, malic, and fumaric acids cannot be used against NH_4OH solns. and the last 2 acids cannot be used in iodometric work. W. T. H.

Contradictions and errors in analytical chemistry. F. L. HAHN. III. The separation of zinc from magnesium, calcium and aluminium by phosphate precipitation. J. DORNAUF. IV. The transformation of alkali sulfates into chlorides. R. ORRO. *Ber.* **55B**, 3434-6(1922).—Voigt (*C. A.* **4**, 443) has effected the sepn. of Zn from Mg, Ca and Al by pptg. the last 3 elements as phosphate in the presence of an excess of NH_4OH . This sepn. works well but to det. Zn it is not sufficient merely to boil off the excess NH_3 from the filtrate to get a complete pptn. of $ZnNH_4PO_4$. The analysis succeeds, however, if the original addition of phosphate is kept small and then, after filtering off the phosphates of Mg, Ca, etc., the filtrate is made acid to methyl red and the $ZnNH_4PO_4$ formed under ideal conditions as recommended by Dakin. The usual method for transforming alkali sulfate to chloride fails to take into account the fact that some alkali chloride is adsorbed by a $BaSO_4$ ppt. unless the soln. is extremely dil. If, however, the alkali sulfate soln. and the $BaCl_2$ soln. are both run slowly in equiv. quantities from a buret into 10 cc. of N HCl soln. which is kept boiling, a ppt. of $BaSO_4$ is obtained which is free from adsorbed alkali salt. W. T. H.

The use of textile fibers in microscopic qualitative chemical analysis. V. The detection of gold by means of stannous chloride-pyrogallol viscose-silk fibers. II. I. COLE. *Philippine J. Sci.* **21**, 361-4(1922).—The reduction of $AuCl_3$ soln. by a mixt. of $SnCl_2$ and $SnCl_4$ leads to the formation of a red or violet color. This fact has been utilized to test for gold by impregnating fibers with the above mixt. and noting under the microscope the effect of a drop of Au soln. on the fibers. Expts. showed that the best method to prep. the test fibers was as follows: Dissolve 10 g. $SnCl_2$ in 95 cc. distd. H_2O and 5 cc. concd. HCl, filter and add 10 g. $C_6H_4(OH)_2$ to the filtrate. Heat viscose-silk fibers in this soln. for 10 min. on the water bath. Remove the fibers, wash well with H_2O and dry between filter paper. No decrease in sensitivity of fibers prepd. in this manner was noted at the end of six mos. To test for Au with the above fiber, place upon an object slide a drop of the soln. to be tested. Insert into it a fiber 5 mm. long for only part of its length. Move the prepn. on the stage of the microscope until a portion of the fiber both in and out of the drop falls within the field of vision. Let the drop evap. spontaneously to dryness. A red to purple color denotes Au. A strong soln. of Au immediately turns freshly prepd. fibers dark red, older fibers dark blue; weaker solns. give a red or blue color upon evapn. of the drop to dryness. Alkali hydroxide prevents the formation of the color. Mineral acids retard the formation of the color. Reducing and oxidizing agents in general interfere. $AgNO_3$ turns the fiber yellow to brown even in the absence of Au; but, unless Ag is present in excessive amts. it does not mask the red color produced when Au is present. Pt salts do not color the fiber. $(NH_4)_2MoO_4$ and $(NH_4)_3PO_4 \cdot 12MoO_3$ turn the fiber a light blue color, readily distinguishable from the dark blue or bluish red obtained when Au is present. This method gave a positive test for a soln. contg. 0.05 g. Au per l. C. E. CARLSON

Sampling of spotty gold ores. C. D. DEMOND AND A. C. HALPERDAHL. *Eng. Mining J. Press* **114**, 948(1922).—By application of the principles of precision of mea-

surements to the formula $W = k D^a$, where W = wt., D = diam. of the largest particle, and k and a are consts. it is shown that any spotty Au ore can be accurately sampled. A certain ore was ground to 0.80 in. and 59 lb. taken as a sample. This was crushed to 30 mesh, riffled to 7.5 lb., and then prepd. through 200 mesh for assay. The results of the assay varied from 0.370 to 1.800 oz. with an av. of 0.628 oz. According to precision of measurements the expected deviation from the av. is 0.426 oz. However, it is desired to know the wt. necessary to give a precision of 0.01 oz. By the laws of probability the deviations are inversely as the square root of the quantity of ore taken. Hence $\sqrt{(W/59)} = (0.426/0.01)$ and, solving, $W = 108,000$ lb. With this wt. the precision will be 0.01 oz. in half the cases. If 2.8 times this last wt. (301,000 lb.) is taken, the deviation will be 0.01 oz. in 90 to 95% of all cases. A quantity of ore was ground to 150 mesh (0.004 in.) and with an assay-ton (0.064 lb.) for analysis the results varied from 0.23 to 0.25 cz. with an av. of 0.238 and an expected deviation of 0.0091 oz. By substituting these values of W and D in the original formula and solving it is found that $k = 576,000$ and $a = 2.90$. From these values is detd. the weight necessary for any given size of this ore. For a 0.25-in. ore 10,300 lb. is required, which this particular mill was not equipped to handle.

C. F. CARLSON

Sampling spotty gold ores. M. W. VON BERNEWITZ. *Eng. Mining J. Press* 114, 1063 (1922).—A note on handling a sulfo-telluride ore.

C. F. CARLSON

The successive electrometric titration of iron, vanadium and uranium. R. G. GUSTAVSON and C. M. KNUDSON. *J. Am. Chem. Soc.* 44, 2756-61 (1922).—Analyses were made of solns. contg. salts of Fe, V and U alone and in combination. These elements can be titrated electrometrically after reduction with Zn and H_2SO_4 but with V the titration must be carried out in an indifferent atm. A mixt. of Fe and U salts may be titrated with $KMnO_4$ after reduction with Zn provided the acidity is kept low (about 5 cc. of concd. H_2SO_4 in 250 cc. of soln.). Fe and V can be titrated similarly in an atm. of CO_2 and with about twice as much acid present. If U is present, the V is obtained from the final step in the titration curve and the U by deducting this value from the first step of the same curve. The detn. of V and U in mixts. is accomplished similarly. When all 3 elements are present, it is best to proceed in the same way but with less acid at the start (4 cc.). After the second inflection, the acid concn. is increased twofold. The V and Fe are represented by the last and next to the last steps and the U is found by deducting the V value as found in the last step from that indicated on the curve between the first and second inflections.

W. T. H.

A new method for the electrometric titration of vanadium in the presence of iron and chromium. H. H. WILLARD and F. FENWICK. *J. Am. Chem. Soc.* 45, 84-92 (1923).—A polarized, bi-metallic electrode system (*C. A.* 17, 37) is a sensitive means for detg. the end-point in the reduction of H_2VO_4 with $FeSO_4$. In $AcOH$ soln. the reduction of 6-valent Cr can be accomplished by H_2O_2 without affecting 5-valent V and the results are better than when HNO_3 is used for the selective oxidation of V. Traces of V may be titrated in the presence of large quantities of phosphotungstate and phosphomolybdate. The procedures recommended for the analysis of steels are as follows: (a) *For V and Cr-V steels.*—A sample contg. about 10 mg. of V is convenient. Place the steel in a 600-cc. beaker with about 25 cc. water and add carefully, from a buret, enough concd. H_2SO_4 to form $FeSO_4$ with all the Fe and about 4 cc. in excess. Heat gently till the sample is dissolved and salts begin to crystallize. Dil. with 20 cc. of hot water and heat till the salts are all dissolved. Add, cautiously, 4 or 5 cc. of concd. HNO_3 and boil. Complete the oxidation with a slight excess of $KMnO_4$ soln. Add sufficient $NaOAc$ to combine with all the excess acid (about 20 g.) and 40-50 cc. of glacial $AcOH$. Add about 0.5 g. of neutralized Na perborate, dil. to 200 cc. and boil 20 mins. Cool to room temp., add 25 cc. of concd. HCl and titrate the H_2VO_4 with 0.02 *N*

$K_2Cr_2O_7$ soln. (b) *For Cr-V-W steels*.—Treat the steel with 40 cc. of 3 N HCl and heat until action ceases. Add 10 cc. of concd. HNO_3 , dropwise at first, and evap. to about 20 cc. Dil. with hot water, filter and wash with hot 2% HCl. Oxidize the filtrate with $KMnO_4$ soln. and add NaOAc, etc., as in (a). (c) *For Mo-Cr-V steels*, proceed as in (a).

W. T. H.

The analysis of alloys containing high percentages of tungsten. K. SEEL. *Z. angew. Chem.* 35, 643-4(1922).—After a discussion of the various methods that have been proposed for analyzing Fe-W and similar alloys, taking into consideration the high price of Pt which makes it advisable to avoid the use of Pt crucibles in procedures where the crucible is likely to be attacked and in labs. where many analyses have to be made, the following procedure is recommended: Carefully fuse 0.5 g. of the pulverized alloy with 6 g. NaOH and 3 g. $NaNO_3$ in a 35-cc. Ag crucible. Cool, ext. with warm water and filter. The filtrate will contain Na tungstate with a little silicate, aluminate and traces of ferrite; on the filter will remain $Fe(OH)_3$ and a little Ag. Dissolve the ppt. in HCl and a little $KClO_4$ in the original casserole and filter again through the same filter. The residue is then AgCl with possibly a little unattacked alloy. (In the latter case, fuse it with $K_2S_2O_7$ in a Pt crucible, ext. the fusion with dd. HNO_3 and ppt. WO_3 by heating. Add this wt. of the WO_3 to that obtained in the main analysis and det. the Fe in the filtrate.) Without paying any attention to any AgCl that may make the soln. cloudy, ppt. the Fe in the HCl soln. by NH_4OH and weigh as Fe_2O_3 . In the alkaline tungstate soln. ppt. $HgWO_4$ with $Hg(NO_3)_2$ in the usual way. After igniting and weighing the residue, ext. the alkali in it by treatments with 7% HCl until it suffers no further loss in wt. Treat the weighed WO_3 with HF to see if it contains any SiO_2 .

W. T. H.

Nickel determination in different kinds of steel. K. CHALUPNY AND K. BREISCH. *Chem.-Ztg.* 46, 1043(1922).—The procedure recommended by Rubricus (*C. A.* 16, 1197) is unsatisfactory in the presence of much Mn, oxides of which ppt., as a result of atmospheric oxidation, in the filtrate from the $Fe(OH)_3$ pptn. That this is actually the case is proved by expts. here described. The electrolytic detn. of Ni in the nical filtrate also fails to give correct values for Ni on account of the presence. It is also inadvisable to attempt to ignite a ppt. of Ni dimethylglyoxime. W. T. H.

The determination of manganese, chromium and nickel in steel. A. EDER AND H. EDER. *Chem.-Ztg.* 46, 1085-6(1922).—The Mn and Cr are detd. in 0.5 g. of steel as described by H. O. Ward (*C. A.* 14, 2769). The Ni is then detd. by KCN titration.

W. T. H.

How the constituent elements of pig iron are determined. I. Silicon and sulfur. W. B. N. HAWK, W. BRADY AND H. E. CAMPBELL. *Raw Material* 5, 420-3(1922).—Detailed directions are given for the sampling of pig iron and for the detn. of Si and S as practised in the laboratories of the U. S. Steel Corp. The Drown method is recommended for Si. For rapid work, the evolution method is recommended for S using 6 N acid to decompose the sample, ammoniacal Cd or Zn soln. or dil. caustic alkali to absorb the H_2S and alkaline $KI-KIO_3$ soln. for the final titration. The gravimetric method for detg. S is also described and recommended for greater accuracy. W. T. H.

An exact, rapid method for determining the sulfur content of iron and steel. F. NICKOLAI. *Chem.-Ztg.* 46, 1025-6(1922).—The proposed method differs from the customary iodometric method in the following details: (1) Only 0.25 g. of sample is taken; (2) the metal is treated with HBr instead of HCl; (3) the evolved H_2S is absorbed by 0.6 N NaOH; (4) after the absorption is complete, the excess NaOH is neutralized with AcOH and the H_2S is titrated directly with I_2 . As evolution flask, a long-necked vessel with bulb holding about 13 cc. is used. By a ground-glass connection, the evolved gas is passed through about 12 cm. of glass tubing to serve as an air con-

denser and then the tubing is bent sharply and ends in a restriction, like that of a wash bottle, at about 15 cm. below the bend of the tubing. Procedure: Place 7 cc. of HBr (d. 1.48) in the flask and 20 cc. of 6 N NaOH in a 70 cc. glass cylinder which is to serve as the receiver in the distn. Pour 0.25 g. of fine sample into the acid and quickly connect the flask with the tubing, sealing with a drop of water. Have the tip of the delivery tubing almost touching the bottom of the cylinder contg. the NaOH soln. Fasten the flask in position and gradually raise the temp. until finally the HBr soln. boils. When no more H_2 is evolved and foaming stops in the evolution flask, lower the cylinder and wash off the tubing. In the analysis of steel samples, 15 min. is sufficient but with cast Fe nearly 20 min. is required to expel all of the S as H_2S . To the alk. soln. add 10 cc. of 25% AcOH and some KI-starch indicator. Allow N/150 I_2 soln. to run into the cylinder from a 4 cc. pipet which is graduated so that the vol. can be read to 0.01 cc., and stop when a permanent blue coloration is obtained. W. T. H.

The separation and determination of sodium and lithium by precipitation from alcoholic perchlorate solutions. H. H. WILLARD AND G. F. SMITH. *J. Am. Chem. Soc.* 44, 2816-24(1922).—The proposed method consists in pptg. and sepg. NaCl from a soln. of $NaClO_4$ and $LiClO_4$ by adding a soln. of HCl in butyl alc. The NaCl is weighed and in the filtrate the Li is detd. as sulfate. If K is present, it is removed first as $KClO_4$ in the usual way. W. T. H.

Methods for the determination of potassium in potash salts. PAUL HUBERT. *Bull. soc. ind. Mulhouse* 88, 500-7(1922).—H. briefly reviews the chloroplatinate, perchlorate, Roger's (C. A. 15, 3044), Sherill's (C. A. 15, 1114) and Przibylla's (Kali 1908, No. 18; C. A. 7, 2024) methods, as regards their suitability for work's control, which requires that they be rapid, accurate and cheap. The last mentioned is the only suitable method. The method is as follows: Dissolve 20-25 g. of the sample in 200-250 cc. of water, filter if necessary, place a suitable aliquot in a dry flask, add a measured amt. of $NaHC_2H_3O_2$ soln. (P. used tartaric acid), shake thoroughly for 5-20 min. at a temp. of 18°, filter, and titrate the filtrate with 0.1 N NaOH. The results vary with the compn. of the salts analyzed; but by analyzing a series of synthetic solns. which contain the same compn. as the various K salts to be analyzed, the relation between the vol. of NaOH and % of K_2O can be detd. for each one of the salts. A. P.-C.

Influence of sodium chloride on the precipitation of copper sulfide. W. BILTZ. *Ber.* 55B, 3393(1922).—Dede and Bonin (C. A. 16, 4155) have called attention to the fact that the pptn. of PbS and CdS is influenced by the presence of NaCl or $CaCl_2$ in the soln. B. and Marcus (C. A. 4, 871) have noticed the corresponding effect in connection with the detection of Cu in potash deposits. W. T. H.

Detection and estimation of lead in some articles of commerce. J. J. HANSSMA. *Pharm. Weekblad* 59, 1314-8(1922).—To detect Pb in imported toys and household articles, heat the object, or a portion thereof, 1 hr. on a water bath with 3% AcOH, treat the soln. with H_2SO_4 , evap. and ignite. Dissolve the residue in NH_4OAc , filter and treat the soln. with K_2CrO_4 . A yellow ppt. which dissolves in KOH indicates Pb. The relative amt. of ppt., considered along with the purpose for which the article is intended, forms the basis for acceptance or rejection on hygienic grounds. A. W. DOX

A rapid volumetric method for the determination of magnesia in carbonate rocks. H. R. BRANDENBERG AND A. H. AVAKIAN. *Concrete* (Mill Section) 21, 78(1922).—Treat 1.0 g. of the sample in a 300-cc. Erlenmeyer flask, fitted with a reflux condenser, with 60 cc. 0.4 N HCl (contg. 2 cc. of alc. phenolphthalein soln. per l.). After boiling and then cooling, titrate the excess HCl with 0.4 N NaOH, taking the first pale pink color as the end point. Boil the mixt. again, add 1.5 g. solid $Na_2C_2O_4$, an excess of 0.4 NaOH, and continue boiling a few minutes. Cool, make up to 200 cc., filter, and titrate 100 cc. of the filtrate with 0.4 N HCl. The calculation is made on the assump-

tion that all the acid consumed in dissolving the substance is due to the presence of CaCO_3 and MgCO_3 , and that in the final pptn., CaC_2O_4 and Mg(OH)_2 are formed.

J. C. WYR

The titration of alkali carbonates in the presence of phenolphthalein. BONNIER. *Compt. rend.* 175, 765-7(1922).—Carbon in a sample of steel is sometimes detd. by absorbing the CO_2 formed by combustion, in a measured vol. of standard NaOH soln. This corresponds to the acidimetric titration of carbonate in the presence of caustic alkali. Warder has recommended titration in the cold with phenolphthalein as indicator but certain difficulties are encountered in getting at the true end point. A series of new expts. show that the following factors do not affect the end point—(1) the presence of excess Na_2SO_4 when the titration is made with H_2SO_4 , (2) varying the temp. between 11° and 30° and (3) the method of stirring. The end point is dependent upon (1) the amt. of indicator used, (2) the rate at which the titration is accomplished and (3) the diln. of the soln. It is recommended to make the concn. of the soln. about 0.01 *N* before titrating, to add 6 drops of phenolphthalein indicator soln. and to add the acid in cubic centimeter portions until near the end of the titration, stirring after each addition, and then finish drop by drop. With these precautions the results should be accurate within 0.1 mg. of C.

W. T. H.

An improved method of analysis for "85% magnesia" covering. H. W. GREIDER. *Ind. Eng. Chem.* 15, 50-2(1923).—The usual proximate method of analysis fails to take into account the fact that the Canadian asbestos fiber is appreciably sol. in water and dissolves considerably in dil. acids. A second and more serious source of error arises from the fact that light Mg carbonate as produced by American manufacturers does not correspond to the formula $4\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 5\text{H}_2\text{O}$. If the empirical factor 0.837 is used for converting $\text{Mg}_3\text{P}_2\text{O}_7$ into the original Mg carbonate instead of 0.872 as required by the above formula, the results of the proximate analysis will be nearer the truth. An improved method of sampling and carrying out the analysis is described and has been adopted by the members of the Magnesia Association of America.

W. T. H.

Volumetric determination of phosphate in solution. F. W. BURY. *J. Soc. Chem. Ind.* 41, 352T(1922).—Phosphates may be titrated with AgNO_3 according to the equation: $3\text{Na}_2\text{HPO}_4 + 6\text{AgNO}_3 = 2\text{Ag}_3\text{PO}_4 + 6\text{NaNO}_3 + \text{H}_3\text{PO}_4$, provided the soln. is kept neutral. For this purpose borax is preferable to ZnO or CuCO_3 . Add a measured amt. of the phosphate soln. to be analyzed to a measured excess of AgNO_3 soln. Run in from a buret 0.1 *N* borax soln. until neutral to litmus. Filter and det. the excess AgNO_3 by the Volhard method or by adding an excess KCl and titrating the excess with 0.1 *N* AgNO_3 using K_2CrO_4 as an indicator.

S. G. SIMPSON

Determination of "mixed acid." W. H. PATTERSON. *J. Soc. Chem. Ind.* 41, 496-7R(1922).—Mixed acid here refers to mixts. of HNO_3 and H_2SO_4 such as are used in nitration, or the spent acid left after nitration. **Total acid.**—Titrate with NaOH using phenolphthalein as an indicator. **Nitrous acid.**—Titration with KMnO_4 is satisfactory for fresh acid. With spent acids in which the HNO_3 content is high and org. matter is present, the KMnO_4 method needs careful control. It may be employed in the analysis of waste acid from TNT manuf. but not from picric acid, for in the latter case oxalic acid is invariably present. To est. HNO_2 alone, add the sample to a strong soln. of K citrate free from carbonate in a Lunge nitrometer. Add a concd. soln. of $\text{K}_4\text{Fe(CN)}_6$. The vol. of NO evolved is a measure of the HNO_2 present. This method tends to give low results. **Total nitrogen acids.**—(1) Nitrometer method. Large errors may occur if the app. is not manipulated correctly and especially if many tests have to be made. Nitrometers should always be constructed with a side tube and cup connected by a two-way stopcock with two diagonal bores. The gas can then always

be expelled through the side tube and each bore of the tap used for one purpose only. About 5 cc. of 90% H_2SO_4 should be used with the sample in the nitrometer. (2) *Reduction to NO*.—With spent acid results by this method agree closely. With fresh acid a result within 0.12% can be obtained by careful measurement. The liability to error is greatest in making a first estn. with a fresh charge of ferrous salt. (3) *Reduction to NH_3* .—Not discussed. (4) *Direct titration with FeSO_4* .—Dissolve the pure crystals in 30% H_2SO_4 . The end-point is taken as the formation of the brown color between FeSO_4 and NO. The conditions necessary to obtain results accurate within 0.1% are as follows: (a) An excess H_2SO_4 must be used; hence mix about 0.5 g. of sample with 100 cc. concd. H_2SO_4 . (b) The flask is kept at a temp. of under 30° in H_2O and agitated during titration. (c) The factor of the FeSO_4 is detd. just before use by standardization against a known amt. of pure nitrate or HNO_3 . (5) *Nitron method*.—Not discussed. (6) *By titration after evapn. of the nitrogen acids*.—Evap. about 1 g. of the sample for at least 30 min. on a water-bath. Add 1 cc. H_2O , stir, and heat for 15 min. more. Titrate the H_2SO_4 using methyl orange as indicator. This can be, but is not always, reliable, the H_2SO_4 content being in some cases more than 0.5% too high. (7) *Double titration*.—Det. total acid by titration of the hot soln. with Ba(OH)_2 using phenolphthalein as indicator. Add a known excess of standard Na_2CO_3 soln., filter, and titrate excess Na_2CO_3 with HCl using methyl orange as indicator. This method tends to give low results for HNO_3 .

S. G. SIMPSON

The role of chromic oxide in sulfochromic oxidation. L. J. SIMON. *Compt. rend.* 175, 768-70(1922); cf. *C. A.* 16, 3282.—Cross and Bevan have recommended detg. C in saccharine materials by treating the org. material for 4 mins. with a mixt. of concd. H_2SO_4 and CrO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ or Ag_2CrO_4 and measuring the vol. of evolved gas. Blank detns. show that this mixt. can be heated for an hr. at 100° without any evolution of O_2 , there is also no O_2 evolved on heating 4 mins. at 110° , but there is an appreciable quantity of gas formed by boiling 4 mins. at 120° and apparently trivalent Cr is capable of catalyzing the reaction. When 12-15 cc. of concd. H_2SO_4 and 4 g. of CrO_3 are used in the test, it requires considerable trivalent Cr to cause an appreciable evolution of O_2 . It becomes appreciable in 4 mins. at 100° only when about 6 g. of chrome alum are added. Upon long boiling, however, all of the CrO_3 may be decomposed. Again, AcOH is not attacked ordinarily by this method of analysis but upon the addition of trivalent Cr it becomes oxidized. Obviously these facts have to be taken into consideration when the C content is detd. by sulfochromic oxidation.

W. T. H.

Gasometric method of estimating the halogen in organic compounds. A. K. MACBETH. *Chem. News* 125, 305-6(1922).—Many compds. contg. an electropositive halogen atom are acted upon by reducing agents such as hydrazine and the halogen removed. When hydrazine is used, the vol. of N_2 evolved is a measure of the halogen present. The detn. is best carried out in a Van Slyke nitrometer using 1 cc. of a 5% hydrazine hydrate soln. Run this soln. into the de-aminizing vessel, turning the 3-way stopcock to allow the displaced air to escape. Turn the tap into connection with the graduated column, introduce 5 cc. of a soln. of the halogen compd. into the de-aminizing vessel and measure the vol. of gas evolved, making the necessary corrections. The time for the reaction varies with the compd. used.

S. G. SIMPSON

Microchemical detection of fumaric acid. L. VAN ITALLIE. *Pharm. Weekblad* 59, 1312-4(1922).—On account of the wide occurrence of fumaric acid in both *cryptogams* and *phanerogams* a reliable qual. test is desirable. The crystals obtained by treating a soln. of NH_4 fumarate with Pb(OAc)_2 or Cu(OAc)_2 are believed to be sufficiently characteristic for microscopic identification.

A. W. DOX

The determination of *d*-tartaric acid. ANDRÉ KLING. *Ann. chim.* 18, 189-216 (1922).—The principle of the new method is that *d*- $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, which is found in natural

products, combines in soln. with an equiv. amt. of l - $H_2C_4H_4O_6$ to form racemic acid. While it is impossible to ppt. quant. d - $H_2C_4H_4O_6$ with Ca or Pb salts, racemic acid is pptd. completely by either in a weakly $HC_2H_3O_2$ soln. The $Ca_2(C_2H_3O_4)_2 \cdot 8H_2O$ crystallizes in fine needles; it is insol. in H_2O , in dil. AcOH, in a soln. of alk. tartrate, in cold dil. soln. of Ca and NH_4 salts as well as in a soln. of $Ca(OAc)_2$. It is sol. in dil. mineral acids as well as in caustic alkali. In dil. H_2SO_4 it reduces $KMnO_4$ proportional to twice the amt. of d - $H_2C_4H_4O_6$ it contains. By its characteristic crystalline form it is easily distinguished from d - or l - $CaC_4H_4O_6$. If an excess of l - $H_2C_4H_4O_6$ is added to d - $H_2C_4H_4O_6$, then $Ca(OAc)_2$, all the acid is pptd. as the racemate contg. certain amts. of the l -tartrate. If the ppt. is dissolved in HCl and then repptd. by adding NaOAc, the racemate is obtained absolutely pure. The proposed procedure is as follows: Take 25 cc. of a soln. contg. less than 1% d - $H_2C_4H_4O_6$, dil. to 150 cc., add successively 25 cc. of l -(NH_4) $_2$ $C_4H_4O_6$ (20 g. per l. with 5 cc. AcH added to prevent molding) and 20 cc. $Ca(C_2H_3O_2)_2$ soln. (120 g. glacial $HC_2H_3O_2$ and 16 g. $CaCO_3$ per l.). Mix with stirring and allow to stand for 30 mins. Filter and add a few drops of the above reagents to the filtrate to make sure pptn. is complete. Wash the ppt. with cold H_2O . Dissolve the ppt. on the filter with 20 cc. of 0.5 N HCl, dil. to 150 cc., add 40 cc. NaOAc and bring to a boil, cool, filter and to the filtrate add a few drops of the above reagents to be sure all the racemate is pptd. Wash the ppt. with cold H_2O and dissolve it in hot 10% H_2SO_4 . Add 10 cc. of 50% H_2SO_4 and titrate with $KMnO_4$. For routine analysis the second pptn. may be omitted if a correction factor is detd. for the l - $H_2C_4H_4O_6$ carried down by the racemate. This method has been tested on pure $H_2C_4H_4O_6$, $NaHC_4H_4O_6$, natural and artificial wines, cider, vinegar, wine lees and neutral esters of $H_2C_4H_4O_6$ with excellent results. Since l -(NH_4) $_2$ $C_4H_4O_6$ is not a common commercial product, directions are given for its prepn. C. E. CARLSON

Identification of small quantities of cream of tartar by microchemical methods. G. DENIGES. *Bull. soc. pharm. Bordeaux* 60, 169-72(1922).—A 0.5-mg. sample of $KHC_4H_4O_6$ finely powd., was divided into 4 equal portions. (a) One portion was placed on a glass slide and dissolved in a droplet of H_2O . On evap. and cooling typical orthorhombic crystals of $KHC_4H_4O_6$ were deposited. The residue was treated with a droplet of $(AcO)_2Ca$ soln. prepd. by dissolving 2 g. of $CaCO_3$ in a mixt. of 10 cc. glacial AcOH and 40 cc. H_2O . At the end of a short time octahedric or bipyramidal crystals of $CaC_4H_4O_6$ formed. This identified the tartrate ion. The K ion was identified by the formation of yellow cubes, octahedrons or dodecahedrons, of K_2PtCl_6 when the residue was treated with a droplet of a 10% soln. of H_2PtCl_6 . (b) A second portion of the material was placed upon a piece of blue litmus paper previously moistened with H_2O . On crushing gently, the paper was reddened at the points of contact, thus demonstrating the acid character of the material. The unaltered powder was scraped off the paper with the point of a knife, spread on a glass slide and treated with a droplet of picric acid soln. (1:100). The formation of long yellow prismatic crystals of K picrate confirmed the presence of K. (c) A third portion was placed on a glass slide and treated with a droplet of resorcinol-sulfuric acid reagent. On heating gently over a low flame a violet-red color developed at 140-150°. This confirmed the tartrate ion.

A. G. DuMEZ

The iodometric determination of sugar. F. AUERBACH AND E. BODLANDER. *Z. angew. Chem.* 35, 631-2(1922).—It is common practice to correct sugar values obtained by iodometric titration so that they will agree with values obtained by weighing Cu_2O . This fails to take into consideration the facts that the gravimetric values are usually a little low for small quantities of invert sugar and the titration values are usually low for large quantities of sugar. An empirical table is given for computing the sugar content on the basis of expts. with known quantities of invert sugar. Even with this

table, considerable practice is necessary in order to be sure of getting consistent results. If the final titration takes place dropwise about 20% less thiosulfate is used in a blank titration than when the titration is accomplished rapidly by adding 2 cc. of thiosulfate at a time.

W. T. H.

Use of sodium 1-naphthol-2-sulfonate for the spectrophotometric estimation of aromatic amino compounds. W. E. MATHEWSON. *J. Assoc. Official Agr. Chem.* **6**, 16-28(1922).—Values are given for the transmissive indices or extinction coeffs. of alk. solns. of the azo dyes formed from aniline, *o*-toluidine, 1-naphthylamine, 2-naphthylamine, benzidine, anthranilic acid, methyl anthranilate, sulfanilic acid and naphthionic acid by diazotizing and coupling with 1-naphthol-2-sulfonic acid. Similar values are given for the transmissive indices of solns. of 4-nitroso-1-naphthol-2-sulfonic acid. These values may be applied to the estn. of small amts. of amines. Dissolve 0.00050-0.00100 g. of the base in 100 cc. of 0.25 *N* HCl and treat at 25-30° with 1 cc. of 0.5 *N* NaNO₂ soln. After exactly 2 min. pour with stirring into a beaker contg. a mixt. of 15 cc. of 5 *N* Na₂CO₃ soln. and 5 cc. of a 5% soln. of Na 1-naphthol-2-sulfonate. Transfer the soln. to a graduated flask, dil. to 150 cc. or 200 cc. and det. the transmittance at 546μ. The colored soln. obtained by this procedure contains in addition to the azo dye a small amt. of the yellow nitroso deriv. but the effect of this on the light absorption is negligible. The dyes are obtained in alk. mixts. contg. NaNO₂ and Na 1-naphthol-2-sulfonate and cannot be conveniently sepd. from these with immiscible solvents. To insure complete diazotization before any appreciable quantity of the diazo compd. has suffered decompn., an amt. of nitrite equal to 0.0005 mol. of nitrite is employed to diazotize 0.00001 mol. of amine. If the carbonate soln. is acidified, the HNO₂ at once reacts with the Na 1-naphthol-2-sulfonate, producing an amt. of new coloring matter very much greater than the quantity of azo dye present. Four cc. of a 3% soln. of hydrazine sulfate may, however, be used to destroy the excess HNO₂ before coupling. Na nitrosomaphtholsulfonate may be used for the spectrophotometric *detn.* of HNO₂. Mix a dil. soln. of the nitrite with 2 cc. of a 5% soln. of the reagent, cool, acidify, let stand 10 min., make alk., dil., and det. the transmissive index. To det. 2-naphthylamine in commercial oil-sol. food dyes, sep. the 2-naphthylamine by dissolving 1 g. of the dye in 50 cc. of benzene and extg. in a separatory funnel with 4 25-cc. portions of 0.25 *N* HCl. Provide a second funnel contg. 50 cc. of benzene and shake out the acid portions separately with this solvent. Treat the soln. of the extd. base in 0.25 *N* HCl at room temp. with 1 cc. of 0.5 *N* NaNO₂ soln. and allow to stand exactly 2 min. Add 5 cc. of a satd. soln. of hydrazine sulfate, stir, allow to stand 1/2 min. and treat with 5 cc. of 5% Na 1-naphthol-2-sulfonate and finally with 15 cc. of a 25% soln. of Na₂CO₃, added quickly and with stirring. A soln. contg. a known amt. of 2-naphthylamine is carried through in exactly the same way and the two solns. are compared colorimetrically.

S. G. SIMPSON

Detection of methanol in liquids containing ethyl alcohol. I. M. KOLTHOFF. *Pharm. Weekblad* **59**, 1268-74(1922).—The delicacy of several modifications of the Denigès test was studied under various conditions of acidity and alkalinity and varying amounts of reagents. Schiff's reagent as prepd. by Elvove (*C. A.* **11**, 1114) keeps for 6 months or longer. In the presence of 10% EtOH the Denigès-Chapin test is sensitive to 0.05% MeOH. The test is applicable to tinctures and alc. beverages, after diln. with H₂O 1:10, without the necessity of distg.

A. W. DOW

Test for acrolein (POWICK) 27. Preparation of sodium bismuth thiosulfate and its use in the determination of K (CUISNIER) **6**. Zirkite ore [analysis of Zr compounds] (THOMPSON) **8**.

HAMILTON, LEICESTER F. and SIMPSON, STEPHEN G. Calculations of Quantitative

Chemical Analysis. New York: McGraw-Hill Book Co. 200 pp. \$2.00. Reviewed in *Chem. Bull.* (Chicago) 9, 257 and *Can. Chem. Met.* 6, 207(1922).

MITCHILL, C. AINSWORTH. Documents and their Scientific Examination. (With especial reference to the chemistry involved in cases of suspected forgery, investigation of disputed documents, handwriting, etc.) London: Charles Griffin & Co. 215 pp. 10s. 6d. Reviewed in *Analyst* 47, 497 (1922).

RÖHM, OTTO. Die Massanalyse. 2nd. Ed. Berlin and Leipzig: Vereinigung wissenschaftl. Verleger. 96 pp. M 12.

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

Iridosmine crystals from Ruby Creek, Atlin district, B. C. T. L. GLENHILL. *Univ. Toronto Studies, Geol. Ser.* No. 12, 40-42(1921).—Iridosmine is found in a black sand, and comes from ultra-basic rocks at the head of Ruby Creek. The forms observed were: c , x , a , and new $h(11\bar{2}3)$, $u(11\bar{2}9)$; $a:c = 1:1.3823$. E. F. H.

The orienting action of the crystal fields of halite and sylvite. F. RINNE. *Centr. Mineral. Geol.* 1921, 577-80.—If a drop of satd. KCl soln. be placed on a cleavage surface of halite, or of NaCl soln. on sylvite, those crystals (cubes) forming in immediate contact with the surface of the mineral take up a position parallel with the supporting cleavage surface. The theory of this phenomenon is discussed. E. F. H.

The production of rose-red coloring in fluorite. C. DOWLER. *Centr. Mineral. Geol.* 1921, 479-80.—Almost colorless fluorite from Weardale became rose red in color on treatment with a quartz lamp for 6 hrs. A much longer (14 days) treatment with $1/2$ g. Ra chloride had no effect on the original color. E. F. H.

Quartz as a geologic thermometer and the significance of the composition planes of its twins. O. MÜGGE. *Centr. Mineral. Geol.* 1921, 609-15, 641-8.—A summary of criteria for the detn. of the temp. of formation of rock crystal is given as follows: I. Crystals without twinned portions, $t < 575^\circ$; II. with twinned portions, a . with trapezohedron or parallelogram faces, α . distribution of such faces conforms to twin boundaries, $t < 575^\circ$; β . the converse, $t > 575^\circ$; b . without such faces, α . end faces regular combinations of + and - rhombohedrons, 1. boundaries regular, $t < 575^\circ$; 2. irregular, $t < 575^\circ$; β . end faces hexagonal pyramids or irregular in size, 1. boundaries irregular, $t \leq 575^\circ$; 2. regular, $t < 575^\circ$. Also in *Nach. Kgl. Ges. Wiss. Göttingen Math. physik. Klasse* 1921, No. 2, 217-22. E. F. H.

Rutile-ilmenite intergrowths. T. L. WATSON. *Am. Mineral.* 7, 185-8(1922).—A vein in Franklin Co., Va., shows rutile intergrown with both primary and secondary ilmenite. Unusually complete analyses of this and several other occurrences of rutile are given. That of the rutile with but little ilmenite showed FeO 2.21% and sp. gr. 4.272. The Fe shown in rutile analyses has been assumed to be present in a tetragonal form of $Fe(TiO_2)$ supposedly isomorphous with $(TiO)(TiO_2)$, but Holden's calcns. of the sp. gr. of the former (C. A. 15, 2602) show a value identical with that of the purer ilmenites. As microscopic study always shows ilmenite, it is concluded that, as has been found to be the case in certain sulfides and in titaniferous magnetites, mechanical admixture rather than isomorphism explains the presence of minor constituents. In rutile, the Fe is due to admixed ilmenite. Cf. following abstract. E. T. W.

Geology of a vein occurrence of rutile-ilmenite in a new locality. T. L. WATSON. *J. Wash. Acad. Sci.* 12, 447-54(1922); cf. preceding abstract.—The rutile-bearing quartz vein occurs in mica schist. The rutile is enclosed in the quartz, as red brown crystals, singly and in groups. The compn. and intergrowth relations are discussed. E. F. H.

The natural iron oxide hydrates. KARL WILLMANN. *Centr. Mineral. Geol.* 1921,

673-8.—W. distinguishes the following as minerals: amorphous "brauneisen," varying in H_2O content; dimorphous cryst. forms of $Fe_2O_3 \cdot H_2O$, "rubinglimmer" and "nadel-eisenerz" or "samblende," the first in red transparent tabular crystals, the second yellow orange and fibrous; and cryst. $2Fe_2O_3 \cdot 3H_2O$, all being optically distinct. E. F. H.

Calcite from Shangoimah Island, near Thunder Cape, Lake Superior. A. L. PARSONS. *Univ. Toronto Studies, Geol. Ser.* No. 12, 51-53 (1921).—The crystals measured were thought to have been formed at the temp. of Lake Superior water in summer, from a soln. of $CaCO_3$ in water containing CO_2 . The following forms were present: (Goldschmidt symbols) $\bar{1}/2$, 1, 4, 41, $7/4$, $1/4$, $\bar{8}2$, $\bar{8}4$, $\infty 0$, ∞ , (new) $48.8/9$, $21.10/9$.

E. F. H.

Analysis of paradoxite from Euha, Saxony. W. SCHÜLER. *Centr. Mineral. Geol.* 1921, 737-8.—The mineral occurred with fluorite in quartz and porphyry veins. The forms present were (110), (101), and (001); sp. gr. = 2.425-2.430. Analysis gave: SiO_2 65.24, Al_2O_3 17.73, FeO 0.14, Fe_2O_3 0.09, K_2O 12.57, Na_2O 1.05, CaO 2.86, MgO 0.24, BaO 0.06, SO_3 0.04, F trace, sum 100.02%. It is practically a K-feldspar.

E. F. H.

Note on a garnet from a pegmatite in Idaho. E. V. SHANNON. *Am. Mineral.* 7, 171-3 (1922).—Analysis of rose-colored garnet from pegmatite showed it to contain 64% almandine, 33 spessartite and 3 pyrope. The n calcd. for such a mixture agreed with the observed value, 1.818.

E. T. W.

A new andalusite occurrence in the Ferwall group (Vorarlberg), and its regional geological significance. H. P. CORNELIUS. *Centr. Mineral. Geol.* 1921, 290-3.—Peach-blossom-red andalusite is associated with quartz veins and lenses in schist at the Reutlinger furnace. It seems to be of hydrothermal origin.

E. F. H.

The state of combination of water in heulandite. A. BEUTELL. *Centr. Mineral. Geol.* 1921, 694-702, 721-34.—Under suitable conditions the dehydration and rehydration of heulandite take place in such a way that the temp.-water content curves are step-like. The mineral contains 11 (2×5.5) mols. of water, and all are present as hydrates.

E. F. H.

The absorption of gases by chabazite. R. NACKEN AND W. WOLFF. *Centr. Mineral. Geol.* 1921, 364-72, 388-94.—An app. for measuring the vol. of gas absorbed by a dehydrated mineral is described. Dehydrated chabazite strongly absorbed air, N , CO_2 , and illuminating gas. For instance, in one expt. chabazite took up 14 times its own volume, or 1.3% by wt. of N . The effect of varying physical conditions is discussed.

Notes on the composition of talc. WM. F. FOSHAG AND E. T. WHERRY. *Am. Mineral.* 7, 167-71 (1922).—Previous analyses of talc show $H_2O : MgO : SiO_2 = 1:4:5$, $1:3:4$ or $2:4:5$. Analysis of samples from Russell, Mass. and Porterville, Cal. gave 4:8:9, but one mol. of H_2O could be driven off at dull red heat without essentially altering the optical properties. Talc containing only firmly bound H_2O is insol. in acids, but sorts contg. also a loosely bound mol. are readily decomposed. It is suggested that the excess H_2O is interlayered with the normal mineral mols. in the direction of the cleavage, being held by electrostatic attraction.

E. T. W.

Notes on Canadian minerals. ANON. *Univ. Toronto Studies, Geol. Ser.* No. 12, 69-72 (1921).—Caledonite is found on Beaver Mtn., the Slocan mining division, B. C.; dumortierite from Ashby, Addington Co., Ont.; stephanite (with analysis) from the Penn. Canadian Cobalt mine, matildite (analysis) from the O'Brien mine; gersdorffite (analysis) Silver Bar mine, Cobalt.

E. F. H.

The inclusions in the basalts between Godesberg and Remagen. CARL SKOBTSCHE. *Centr. Mineral. Geol.* 1921, 353-63; The minerals in the inclusions in basalt from Finken-berg, near Beuel. C. WURM. *Ibid.* 1921, 581-90.—The following minerals occur as inclusions, most of them being common to both localities; their origin and the changes

wrought in them after their inclusion in the magma are discussed: Quartz, orthoclase, plagioclase, garnet, wollastonite, nosean, zircon, scapolite, epidote, cyanite, sillimanite, andalusite, cordierite, corundum, spinel, olivine, augite, diopside, bronzite, hornblende, biotite, apatite, titanite, graphite, copper, magnetite, ilmenite, sphalerite, molybdenite, chalcocopyrite, pyrrhotite, marcasite, pyrite, gypsum, natrolite, apophyllite, phillipsite, chabazite, siderite, calcite, aragonite, barite, chalcedony, opal; also trachyte rock.

E. F. H.

The tellurides. T. A. RICKARD. *Eng. Mining J.-Press* **114**, 708, 752, 972-3 (1922).—The geographic occurrence, details of discovery, and data on value as ores are given for the tellurides of Au, Ag, Pb, Ni, Cu, Bi and Hg, and for tellurite.

E. F. H.

A preliminary study of zirkite ore. J. G. THOMPSON. *J. Phys. Chem.* **26**, 812-32 (1922).—Zirkite (baddeleyite) ores are studied with a view to improving their refractory properties by the elimination of certain impurities. 90-95% of the SiO_2 in the raw material may be removed by heating a mixt. of the ore with just enough coke to convert the Si to the carbide, in an electric furnace, to a temp. above 2220° . With C in excess, the removal is incomplete. If the Fe be then removed by treatment with Cl or phosgene, zirconia sufficiently pure for refractory purposes might be obtained. Methods of analysis of Zr compds. are briefly reviewed, and a scheme for the detn. of Zr, Si, Fe, and Ti is outlined.

E. F. H.

Geology of the Moorlands (S. Australia) brown-coal deposits. A. C. BROUGHTON. *Trans. Proc. Royal Soc. S. Australia* **45**, 248-53 (1921).—The brown coal was deposited in swamps. Several analyses are given.

E. F. H.

The origin of petroleum. H. HÖFER. *Petroleum Z.* **13**, 1301-2 (1922); cf. *C. A.* **16**, 2099.—A study of American petroleum indicates that the paraffin oils are the oldest, the naphthene oils the youngest and the various mixts. occur chronologically between these two. All petroleum is of fatty origin, and was formed at relatively low temps. and high pressures. The variations in time and pressure allowed other influences, as oxidation, diln., polymerization, etc., to be exerted, whereby a variety of products were formed.

D. F. BROWN

The physical chemistry of the crystallization and magmatic differentiation of igneous rocks. V. J. H. L. VOOR. *J. Geol.* **30**, 611-630 (1922).—The influence of pressure is discussed. In deep-seated rocks the rise of the melting point of rock-forming minerals is inconsiderable. Many minerals such as olivine, monoclinic pyroxene, feldspars, spinel, magnetite, etc., can form under either low or high pressures. Melilit is found only in extrusive types (low pressure) the corresponding intrusives containing instead olivine and anorthite-hytownite. Likewise the leucite in low-pressure rocks is replaced by microcline and biotite. The formation of garnet is favored by high pressure. VI. *Ibid* 659-72.—The influence of the light volatile compds. as H_2O , CO_2 , etc. is discussed. During crystn. the vol. material will be disposed of as follows: Some will escape if the pressure is high, some will be included in the minerals as inclusions, some may enter in solid soln., some may enter the crystg. minerals as H_2O in micas, the rest will remain in the magma and be concd. in the mother liquid. It is estd. that 4% indicates the max. original content of H_2O in the parent magmas.

W. F. HUNT

Graphic study of igneous rock series. F. F. GROUT. *Bull. Geol. Soc. Am.* **33**, 617-38 (1922).—The nature of differentiation in 40 rock masses is shown by diagrams based on alkalis and SiO_2 . Some of the conclusions are: (a) magmas need not be of any particular compn. in order to develop into a differentiated series, (b) the trend of differentiation is in different directions in different localities even when the magmas are similar, (c) nearly all alkaline rock masses have some phase near the av. nephelite syenite, (d) the primary magma approaches av. basalt but varies considerably.

W. F. HUNT

The nephelite syenite and nephelite porphyry of Beemerville, New Jersey. M. AUROUSSEAU AND H. S. WASHINGTON. *J. Geol.* 30, 571-86(1922).—The nephelite syenite is interpreted as a sill or flat laccolith of foyaite intruded by dikes of nephelite porphyry and leucite tinguaita. The nephelite syenite is characterized by low SiO_2 (47.19), equal amts. of Na_2O and K_2O (7.97 and 8.23), high content of TiO_2 (2.16) and ZrO_2 (0.13). It is also shown that the nephelite porphyry is not a Sussexite as formerly supposed. The occurrence of Zr and rare earths is rather widespread, especially in the region east of the Appalachians.

W. F. HUNT

Petrography of the South Shetland Islands, the Palmer Archipelago, and the Danco Land coast, Graham Land, Antarctica. G. W. TYRRELL. *Trans. Royal Soc. Edinburgh* 53, pt. 1, 57-79(1922).—The plutonic rocks of Graham Land and adjacent islands are calcic, and include adamellite, tonalite, quartz-diorite, quartz-pyroxene-diorite, quartz-gabbro, gabbro, and olivine-gabbro. The abundant aplitic and porphyritic rocks are of the same character. The volcanic rocks of the South Shetland Islands are mainly andesites, with bandaite, dacite, trachyandesite, rhyolite, and olivine-basalt. The modes of many of these rocks were measured by the Rosiwal method, and the corresponding compns. calcd.

E. F. H.

Volcanic ash bed in the Ordovician of Tennessee, Kentucky and Alabama. W. A. NELSON. *Bull. Geol. Soc. Am.* 33, 605-15(1922).—A greenish, sticky, clay-forming bed, detd. as bentonite, an altered rhyolitic volcanic ash, is thought to have covered an area approx. 800 mi. in length and 450 mi. wide. The volcano producing this ash deposit was located E or NE of High Bridge, Ky. The material swells when placed in water and breaks down into a doughy mass with imbedded sand grains. It contains feldspar and other minerals, chiefly *leuczerite*. SiO_2 58.88-54.50, Al_2O_3 24.85-19.97, Fe_2O_3 1.91-0.51, FeO 1.08-0.45, CaO 1.20-tr., MgO 5.08-2.36, P_2O_5 0.17-0.13, P 0.13-tr., K_2O 4.30-2.04, Na_2O 4.12-1.66, H_2O (100-110°) 6.62-3.44, H_2O (above 110°) 5.40-5.03%. When boiled with H_2SO_4 bentonite loses its colloidal properties and 85% of the Al_2O_3 goes into soln. as $\text{Al}_2(\text{SO}_4)_3$. Bentonite in contact with pyritiferous rocks would be acted upon by the ground waters and the $\text{Al}_2(\text{SO}_4)_3$ might be pptd. by natural reducing agents as tannic acid or acid peat-forming bacteria, producing *banxite* deposits.

W. F. HUNT

Geological memoranda. II. W. HOWCHIN. *Trans. Proc. Roy. Soc. S. Australia* 45, 25-35(1921).—This paper includes an analysis of a *scoriaceous rock*, not of volcanic origin, but probably formed in a bush fire.

E. F. H.

The chemistry of the earth's crust. H. S. WASHINGTON. *Smithsonian Rept.* 1920, 269-319(1922).—The conditions prevailing in the earth's interior are briefly discussed, followed by a description of the general character of igneous rocks. The number of essential rock-forming minerals is small; they are silicates of Al, Fe, Mg, Ca, Na and K. The maxima and the usual range of the principal rock constituents are as follows: SiO_2 , max. 99%, usual range, 75-84; Al_2O_3 , 60, 20-10; Fe_2O_3 , 88, 15-0.5; FeO 35, 15-0.5; MgO , 49, 25-1; CaO , 23, 15-0; Na_2O , 19, 15-0; K_2O , 18, 10-0; H_2O , 10, 2-0; TiO_2 , 70, 2-0; P_2O_5 , 16, 1-0; MnO , 2, 0.3-0. An estimate of the av. compn. of igneous rocks, based upon 5159 "superior" analyses is given: SiO_2 59.09, Al_2O_3 15.35, Fe_2O_3 3.08, FeO 3.80, MgO 3.49, CaO 5.08, Na_2O 3.84, K_2O 3.13, H_2O 1.14, TiO_2 1.05, P_2O_5 0.30, MnO 0.125, CO_2 0.102, ZrO_2 0.039, S 0.053, Cl 0.056, F 0.078, Cr_2O_3 0.056, V_2O_5 0.032, NiO 0.025, BaO 0.055, SrO 0.022, Li_2O 0.007%. This approximates to a granodiorite. The av. compn. of the earth's crust by elements is estd. as: O 46.43, Si 27.77, Al 8.14, Fe 5.12, Ca 3.63, Na 2.85, K 2.60, Mg 2.09, Ti 0.629, P 0.130, H 0.127, Mn 0.096, F 0.077, Cl 0.055, S 0.052, Ba 0.048, Cr 0.037, Zr 0.028, Co 0.027, V 0.021, Ni 0.019, Sr 0.018, Li 0.003, Cu 0.002, Ce etc. 0.001, Be 0.00xx, Co 0.00xx B 0.000x, Zn 0.000x, Pb 0.000xx, As 0.000xx, Cd 0.000xx, Sn 0.000xx, Hg

0.0000xx, Sb 0.0000xx, Mo 0.0000xx, Ag 0.0000xx, W 0.0000xx, Bi 0.0000xx, Se 0.0000xx, Au 0.0000xx, Br 0.0000xx, Te 0.0000xx, Pt 0.0000xx, sum 100%. The elements are referred to two main groups in the periodic table: the petrogenic elements, abundant in igneous rocks, of low at. wt., normally occurring as chlorides, fluorides, oxides or silicates; and the metallogenic elements, rare in igneous rocks, occurring as ores, of high at. wt. and forming in nature "native" metals, sulfides, arsenides, bromides, etc. The suggestion is made that beneath a silicate crust of petrogenic elements is a zone essentially of Ni-Fe, and beneath this a core of metallogenic elements. In igneous rocks and minerals the elements show a correlation of occurrence, oxides of Si, Al, K, and Na tend to go together; Mg, Fe; K, Mg; Na, Fe; Na and Li, Zr, Ce, Cl, F; Mg and Pt, Cr. The idea of comagmatic regions is discussed and some are briefly described. The calcn. of rock ds. from their compn. is discussed, and the av. ds. of the continental masses and ocean floors are calcd. and shown to stand in inverse relation to their elevations. This is confirmative of the theory of isostasy.

E. F. H.

Mass distribution in the interior of the earth compared with the structure of certain meteorites. V. M. GOLDSCHMIDT. *Naturwissenschaften* 10, 918-20(1922).—It is unlikely that below the outer crust in the eclogitic shell extending from 120 km. to 1200 km., mixts. of silicates and Ni-Fe exist in a stable condition. It is more likely that only solid silicates exist in a high state of compression with d. 3.6-4. Isostatic equalization at the boundary of the silicate and eclogitic shells may occur with changes in temp. and pressure. Volcanic action may occur at this boundary due to fusion of the eclogite and transformation to basaltic magma. From 1200 to 2900 km. it is assumed, contrary to most theories, that a shell composed of sulfide and oxide ores exists with d. 5-8. Fe sulfides and magnetite predominate, with smaller amts. of chromite, Ti-Fe, rutile and various sulfides. Below 2900 km. is a metallic core of Ni-Fe. This structure is inevitable if it is assumed that the earth was once liquid, since a mixt. of silicates, sulfides and Fe forms 3 layers when fused. The scarcity of heavy metals in the outer shell is due to their being more easily reducible than Fe because of their greater affinity for S or of a high m. p., and because of their sinking to the interior layers in a manner analogous to the slag, mat and metal in metallurgy. It is suggested that meteorites have solidified with sepn. of their component parts, in a similar manner. No combination of metals corresponding to the eclogitic shell of the earth is found, however, on account of the lack of necessary pressure in the relatively small meteorites. The presence of diamond is due to their formation in a manner like that of Moissan's expts. and not to pressure alone.

C. C. DAVIS

Minerals deposited by bacteria in mine waters. J. PARRY. *Chem. News* 125, 225-8, 240-3, 257-60(1922).—An unusual mineral deposit from the De Beers and Kimberley mines, S. Africa, is described. Coatings of black, brown, or red, sometimes lustrous material were deposited on rocks and wood, and as a core in a pipe, from dripping water. This contained 82-90% CaCO₃, 5-9 MgCO₃, 1.7-2.7 org. matter, and SiO₂, Fe₂O₃, Al₂O₃, H₂O, and Na₂SO₄ (6 analyses given). The water from which it was derived had (pts. per 100,000): CaO 3.08, MgO 1.00, Na₂O 339.60, K₂O 1.41, SiO₂ 2.70, Fe₂O₃ + Al₂O₃ 1.70, CO₂ 58.96, SO₂ 300.09, Cl 34.00, sum 734.88, with org. matter. The large proportion of CaCO₃ in the deposit as compared with the amt. in the water was explained by the discovery that the deposition was due to bacteria which withdrew CaCO₃ into their tissue, and built up the deposit layer by layer. The unusual color was due to cellulose material derived from decaying timbers in contact with the alk. waters.

E. F. H.

Note on the formation of the Alsatian potash basin. RAOUL LEBRUN. *Bull. soc. ind. Mulhouse* 88, 508-11(1922).—The basin consists essentially of 2 potash layers

which are worked and between which are: an unworked deposit of high-grade K salt 0.80 m. thick, a layer of almost pure K salt 0.30 m. thick and 1.80 m. above the first and lying between 2 layers of shale, layers of shale and salt of varying thicknesses, a 10-m. layer of rock salt just below the upper of the two worked deposits, and above and below the potash layers are alternating layers of rock salt and of shale. From a detailed examn. of the fissures in the shales, L. concludes that the K deposits were not formed in a continuous manner but are the result of the leaching of considerable dry marine deposits, the waters having flowed to what is now the Alsatian basin, where they were evapd.

A. P.-C.

ARTINI, E. *Lezioni di mineralogia e materiali da costruzione*. Milan: Libreria Editrice Politecnica E. Tamburini. L 50. Reviewed in *Scientia* 32, 57(1922).

BRAUNS, R. *Mineralogie*. 5th Ed. Berlin: Vereinigung wissenschaftl. Verleger. 146 pp. M 18.

JOHANSEN, ALBERT. *Essentials for the Microscopical Determination of Rock-forming Minerals and Rocks*. Chicago: The Univ. of Chicago Press. \$2.10. Reviewed in *Eng. Mining J.-Press* 114, 775(1922).

WINCHELL, N. H. AND WINCHELL, A. N. *Elements of Optical Mineralogy. An Introduction to Microscopic Petrography*. 2nd Ed. Revised and enlarged. Part I. Principles and Methods. New York: John Wiley & Sons, Inc. \$3.50. Reviewed in *Eng. Mining J.-Press* 114, 1082(1922).

9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

A continuous alkalinity indicator for flotation pulp. B. H. McLEOD. *Eng. Mining J.-Press* 114, 991(1922).—The app. is devised for an acid ore pulp which has to be rendered slightly alk. with CaO for the highest recovery. It consists of a filter placed at the head of the flotation machine and connected by Cu tubing to a glass indicator tube contg. phenolphthalein; fused to the inner surface of the tube. This indicator tube is connected to a bottle which in turn is connected to a vacuum line. When the vacuum line is opened the H₂O in the pulp is filtered through the filter bag and indicator tube into the container. If the water is red, the pulp is alkaline and the intensity of the color depends on the amt. of excess lime. A stopcock is introduced between the filter and indicator tube so the latter may be shut off and low pressure air or H₂O may be turned on to clean the slime cake off the filter bag every few hrs. C. E. CARLSON

Improved flotation machine. W. I. NELSON. *Eng. Mining J.-Press* 114, 1079 (1922).—An arrangement of baffles added to the spitzkasten of Minerals Separation machines gave a concentration 2% higher in Cu without decrease of total recovery.

A. BUTTS

Leaching copper ore with sulfur dioxide. ANON. *Chem. Met. Eng.* 27, 989 (1922).—The history of the experimentation with this process is given. The reagent cost in SO₂ leaching would be only 15% of that in H₂SO₄ leaching. Cf. C. A. 16, 2467.

A. BUTTS

Tests with a view to obtaining copper-nickel mats in the Urals. Y. Y. SRDNIX. *Communications travaux tech. sci. Rép. Russe* 5, 124(1921); *Rev. Métal* 19, 568(Abs.) (1922).—In 1916 the Revdinsky works began a study of the utilization of Ni (0.86%) and Cu (1.5%) ores, with the ultimate aim of finding if it would be possible to work them up electrolytically and more immediately to produce a Cu-Ni mat. A special crucible furnace having a section of 1 m. × 1 m. and a height of 10 m. was constructed, in which were treated in all 130 t. of ore and flux. Wood charcoal was unsatisfactory.

With coke the mat could be satisfactorily sepd. from the slag, which held back traces of Ni and 0.12-0.23% Cu. The mat. contained 2.81% Cu and 1.13% Ni. The ratio of Ni ore to Cu pyrites was gradually increased to 1:1.2. The final charge tested consisted of Cu pyrites 270, Ni ore 330, slag from reheating furnace 220, CaO 80, and coke 125 kg. The test was considered successful. A. P.-C.

Possibilities of technical extraction of vanadium from Russian raw materials. Z. S. KOLOVROT-TCHERVINSKY. *Communications travaux tech. sci. Rép. Russe* 5, 108-9 (1921); *Rev. métal* 19, 568 (Ahs.) (1922).—V deposits of com. value are to be found in the Fergan district. The minerals in the ore contain 16.5 and 12% of V, and the ore (according to a Petrograd analysis) 3.36% V. The ore is being worked up for Ra; V and U will be obtained as by-products, being pptd. from the solns. obtained on the preliminary acid treatment of the ore. A. P.-C.

Objections to the King method of pyritic smelting in a reverberatory. W. M. JOHNSON. *Eng. Mining J.-Press* 114, 1062(1922).—In pyritic smelting there is only a small margin of heat generated; this disappears if there is too much slag or if the heat is poorly utilized. The latter is true of the King reverberatory, wherein the hot gases do not percolate through the charge, but rush directly over the hot slag to the exit flue. A. BUTTS

Oxidation of ferrous salts by atomized air in acid solutions thought practicable. WM. E. GREENAWALT. *Eng. Mining J.-Press* 114, 933(1922).—The oxidation should be possible in a hot solu., working under pressure. CuSO_4 is not affected by SO_2 or CO ordinarily, but under heat and pressure metallic Cu is pptd. by either. An app. is described for causing an intimate mixt. of liquid and gas. A. BUTTS

A wood-burning furnace for smelting cyanide precipitate. M. B. EVANS. *Eng. Mining J.-Press* 114, 1078(1922).—The fire-box has a step grate, so that the bed of coals is kept open though deep. The gas produced from the wood passes through ports where it mixes with auxiliary air, making a very long, intense flame. Smelting takes only $\frac{1}{4}$ as long as with an oil-fired furnace, and the work is easier. A. BUTTS

Blast-furnace waste heat utilized. HUBERT HERMANN. *Blast Furnace Steel Plant* 10, 531-4(1922).—Of the total heat introduced into the blast furnace 40% is consumed in the furnace and 60% leaves as waste gases. Diagrams and heat balance sheets show the distribution of the utilization of the heat from a blast furnace and from a coke oven with and without the use of producer-gas installations. The use of gas engines is recommended and the heat balances are constructed on this basis. The efficiency of these engines where the power can be used is far greater than the burning of the gas under a boiler. W. A. MUELLER

New Claire furnace. GEO. F. TEGAN. *Iron Age* 110, 1422-3(1922).—No deviations from standard practice have been made in the construction of the new furnace. The furnace stands 87 ft. high with a diam. at the hearth of 16 ft. 3 in. and at the bosh of 20 ft. and has a capacity of 500 tons. Three stoves of 2-pass side-combustion types, 100 ft. high and 22 ft. diam. are used in connection with the furnace. The chimney for the waste gases is of concrete and is lined with radial firebrick its entire length of 200 ft. The molten slag is run into a trough with a stream of water and thereby granulated then swept by water through a pipe line under the river to a place 1500 ft. away for disposal. W. A. MUELLER

Cupola malleable production. C. C. HERMANN. *Foundry* 50, 952-5(1922).—The cupola process for the manuf. of malleable iron is cheapest in first costs and more economical in fuel costs. The different kinds of scrap to be used are discussed. It is recommended that the entire output of the cupola be tapped at once into a large bull ladle in order to insure mixing of the iron. In the annealing of the cupola malleable, a temp. of from 200 to 300 deg. F. higher is required than for the annealing of air-furnace iron. W. A. MUELLER

A new cupola lining. KARK GROCHOLL. *Die Giesserei; Iron Age* 110, 1279 (1922).—In Germany a loose refractory mixt. is being used for ramming up the cupola lining, instead of fire brick and blocks. The cost is only $\frac{1}{10}$ of that of firebrick. Patching is done after every heat, with unskilled labor, and a new lining is not required within 2 yrs.

A. BUTTS

Unsolved and solved problems in the technic of iron foundries. L. SCHMID. *Gieserei Z.* 9, 489-93, 499-500, 511-2 (1922).—A long discussion of the economic and chem. difficulties in producing a satisfactory cast Fe with inferior raw material and fuel. Some of the more important processes recently devised to improve efficiency are described in detail with data.

C. C. DAVIS

Foundry coke. A. D. YOUNG. *Colliery Guardian* 124, 1147 (1922).—General results of foundry coke expts. are described. The chief requisites for foundry coke are a max. area of cell surface but a small size of individual cells. It should have a well developed hard cell structure, be non-friable and have high C content, low ash, low S and low P. If too small, clogging of the cupola occurs. By removing all small coke, a better Fe/coke ratio is attained. First-class coke should be silvery-white, dense, with a metallic ring, should not break when falling, and should not contain over 8% ash, 3.5-4% H_2O , 0.8% S or 0.04-0.05% P. Second-grade is darker, more bony and porous, less resistant to pressure, and should contain not over 10-11% ash, 8-9% H_2O , or 1-1.1% S. Third-grade is a lusterless gray-black color, soft, breaking easily where struck, highly porous, holding H_2O tenaciously, a low d., 9-9.5% ash, 13-15% H_2O and 1% S. There should be a min. radiating space to output and max. contact between charge and hot gases per time unit. In high and narrow cupolas, the path of the gases is longer and the velocity greater, and such cupolas are therefore preferable. The heat loss in unburnt gases cannot be wholly eliminated, but can be lessened by guarding against insufficient blast, improper settling of charge and faulty distribution of air at the tuyères.

C. C. DAVIS

Core-oven loss. C. F. MAYER. *Foundry* 50, 839-43, 887-89 (1922).—Extensive tests were made on 2 electrically heated and one oil-fired core oven. The results obtained are analyzed to det. the efficiency of the ovens and the relative heating costs. The data given on baking results enable the foundryman to calculate fuel costs and compare electric with other heating systems based on the cost of fuels in his locality.

V. O. HOMERBERG

The reduction of metallic oxides by means of hydrogen and carbon monoxide. GEORGES CHAUDRON. *Chimie et industrie* 8, 950-64 (1922).—A review of the mechanics of the reversible reactions $Fe + H_2O = FeO + H_2$ and $Fe + CO_2 = FeO + CO$ and their relation to the dissociation of FeO , H_2O , and CO_2 , the application of these results to the purification of steel (H. LeChatelier, *Rev. métal.* 1912, 512), measurement of the equil. of the system $M-MO-H_2O-H_2$ (G. Chaudron *C. A.* 8, 3539), measurement of the equil. of a mixt. of CO and CO_2 (*C. A.* 16, 212, 1192), and the change in compn. of the gases at various points of the blast furnace (Matsubara, *C. A.* 15, 1683).

A. P.-C.

Converter makes better steel. R. BURKE. *Foundry* 50, 915-7 (1922).—The successful operation of the converter depends on the purity of the stock on hand and the absence of oxides in the finished blow. The steel flows better and makes much better castings when it is free from oxides, can be poured at a lower temp. and produces castings more free from blow holes. Fe-Si and Fe-Mn are used as the deoxidizers. Fe-Mn is added in the converter and Fe-Si in the ladle.

W. A. M.

Various fuels used for heating Martin furnaces. BOURG. *Rev. métal.* 19, 539-49 (Abs.) (1922).—An outline of what has been done in various countries towards the use of coke-oven gases and tar for heating Martin furnaces.

A. P.-C.

Use of coke-oven gas for heating Martin furnaces. JEAN DUPUIS. *Rev. métal.* 19, 590-9(1922).—The advantages of the use of coke-oven gas for heating Martin furnaces are elimination of gas producers, and easy maintenance of the high temp. required. These gases, however, should not be preheated, as the hydrocarbons decompose with deposition of C. This does not entail any great loss, because: (1) the temp. of combustion of unpreheated coke-oven gas is about 200° higher than that of preheated producer gas; (2) coke-oven gas constitutes only 15% of the heating mixt. and preheating the air is sufficient. At the Cockerill plant, at Seraing, the use of coke-oven gas gave an increase of 25% in output and decrease of 30% in the consumption of cast iron. The effects of the addition of small amts. of coke-oven gas to producer gas for Martin furnaces was investigated at the Saint-Jacques plant of the Cie des Forges de Châtillon, Commeny et Neuves-Maisons, more particularly to avoid deposition of C. The addition of CO₂ to form CO ($C + CO_2 = 2CO$) is not successful, because the rate of the reaction is too slow. Let $R = (\text{Wt. of oxidizable C—wt. of C formed by dissociation}) / \text{wt. of C formed by dissociation}$. Then: (1) if R is negative, there will be deposition of C; and for any given gas the C deposit will decrease as the algebraical value of R increases; (2) the higher the hydrocarbon content of the gas, the greater the value of R for which the deposition of C will be eliminated. These two results are borne out by tests which are described in detail. With mixts. contg. relatively small amts. (about 20%) of coke-oven gas, the value of R necessary to prevent deposition of C is easily attained if the mixt. contains but a small amt. of water (dew-point about 50–60°).
A. P.-C.

Effect of temperature in the manufacture of steel. CH. CLAUDEL DE COUSSERGUES. *Rev. métal.* 19, 639-44(1922).—In order to have low cost of production and at the same time a high-grade product: (1) A high temp. (above 1600° for basic processes) should be reached as rapidly as possible so as to facilitate the formation of the slag and the oxidation of the metal bath; in the Thomas process part of the charge is blown very hard, while in the Martin and elec. processes part of the charge is fused with the materials required for the formation of the slag. (2) The temp. is reduced (slightly above the fusion temp. of 0.800% C steel) by addition of the remainder of the charge (with addition of a small amt. of O if necessary); the P then acts as a deoxidizer in the presence of the C, and is thus removed. (3) Finally the slag is removed, the excess C is removed, and the deoxidizers (Si, Mn, Al) are added, the temp. being again increased if a very fluid bath is required.
A. P.-C.

Comparison of American and English method of producing high-grade crucible steel. T. H. NELSON. *Trans. Am. Soc. Steel Treating* 3, 279-98(1922).—Eighty % of crucible tool steel made in Sheffield is produced in coke-hole furnaces using clay pots. The 2 processes differ in 5 essentials: source of heat, furnace design, crucible pot, hammering vs. blooming of the ingot, and raw material used. The Am. production is more elaborate and scientific but often produces an inferior quality of steel because of the base metal used and the high tonnage demand. Am. iron is not equal to Swedish iron for a base. Using the same quality of raw material the Am. practice will produce an equally good quality of steel at an increased tonnage. The manuf. of clay pots, methods of deoxidation, furnace design and operation, teeming, and methods of testing are discussed. Several analyses of different grades of steel are given. W. A. MUDGE

Manufacture of alloy steel for airplane shafts. E. KOTHNY. *Chem. Met. Eng.* 27, 1020-4(1922).—An account is given of the manuf. of Ni-Cr steel in the basic Heroult furnace. In order to produce airplane shafting with no trace of transverse structure, it is necessary to use very good raw material and to refine with 2 oxidizing slags as well as the usual carbide slag.
V. O. HOMERBERG

Temperatures at which physical changes occur. H. D. HIBBARD. *Iron Age* 110,

1492-3(1922).—Temps. are listed which relate chiefly to steel production, its heat treatment, and the fusibility of steel and its components. Differentiation is made between actual fusing points and the temps. causing sintering, softening, fluidity, and mobility for handling.

W. H. BOYNTON

The fatigue of metals. LEONARD BAIRSTOW. *Beams* 11, 653-731(1922).—The complete recovery of metals from stress may take months; 10 min. boiling in water accelerates recovery. Two types of fatigue tests are given. In the first, a load is applied at the end of a horizontal specimen caused to rotate at 1000 r.p.m. Rotation continues till the specimen breaks. Results are given for a normal carbon steel, which appears to be unbreakable below stresses of 25 tons per sq. in. The second method insures uniformity of tension and compression by oscillatory motion of specimen and load. Formulas for stress and its limits are given. A table gives results showing relationship between fatigue and compn. B. claims that fatigue tests are more reliable than the extensometer method. Fatigue method detcs. so-called unknown factors allowed for in calcg. max. loads. Results of fatigue tests on Fe and steel show how the form of the specimen affects its strength. Consideration is given to the effect of overstrain on the cryst. material. Diagrams show the formation of slip lines due to strain in crystals, their relation to fatigue and the development of a crack in the metal.

A. H. DICK

Polishing aluminium and its alloys for metallographic study. E. H. DIX, JR. *Chem. Met. Eng.* 27, 1217-20(1922).—A detailed method is given for polishing Al and its alloys in order to obtain a scratch-free surface. Excellent photomicrographs, which show the various constituents obtained by polishing without subsequent etching, are given. A description of the various constituents in Al alloys is given.

V. O. H.

Equilibrium diagram of the iron-carbon system. K. HONDA. *Chem. Met. Eng.* 27, 1180-2(1922).—See C. A. 16, 2293.

V. O. H.

The ternary system iron-boron-carbon. R. VOGEL AND G. TAMMANN. *Z. anorg. allgem. Chem.* 123, 225-75.—The differences between the constitution diagrams for Fe-B alloys reported by Hannesen (C. A. 9, 1452) and Chieyevski and Herdt (C. A. 10, 2569) are due principally to the different rates of cooling used. Since the rates of the latter were the slower, equil. must have been more nearly attained. Their results were used, with the Fe-C diagram drawn by R. Ruer (C. A. 12, 2524), for the construction of a theoretical diagram to show the constitution of the Fe-B C alloys both immediately after solidification and at room temp. Similar diagrams were drawn from data obtained from cooling curves of alloys. For the extensive description and discussion of the properties of the alloys revealed by these diagrams, the original article must be consulted. The difference in hardness between alloys contg. 0-1.0% C quenched from 1000° and slowly cooled, increased with the B content up to 0.02% B. The hardness of the slowly cooled alloys was independent of the B content. The effect of small addn. of B on the hardness of quenched steels is great and is especially pronounced in steels contg. less than 0.3% C. 0.02% B marked the upper limit at which addn. of B could be made without visibly affecting the structure of the alloy.

F. P. FLAGG

Foreign pig iron generally satisfactory. W. A. BARROWS, 3RD. *Iron Age* 110, 1631-2(1922).—Analyses of results obtained from the use of various grades of imported metal in American melting practice indicate uniformly successful application.

V. O. HOMERBERG

The problem of pig-iron specifications. WM. R. WEBSTER. *Raw Materials* 5, 389-90(1922).—Chem. requirements of pig Fe ordered by foundries making the same grade and wt. of castings vary considerably and cause the blast-furnace men unnecessary trouble, as they are called upon to make several grades of pig Fe for the same wt. and grade of casting.

V. O. HOMERBERG

Physics of cast iron. R. MOLDENKE. *Raw Materials* 5, 391(1922).—The production of good castings involve the use of the best materials suited to the production of the castings wanted, the employment of a correct melting, molding, and finishing process, gating the molds correctly, so that the good materials, properly manipulated, may be given the best chance possible to produce good work. V. O. HOMERBERG

Non-metallic inclusions and ferrite segregation in steel. I. G. MAHIN AND H. W. BOTTS. *Chem. Met. Eng.* 27, 980-5(1922).—It is believed that the influence of non-metallic inclusions upon ferrite segregation in slowly cooled hypoeutectoid steel is principally due to the fact that the inclusions are centers of contamination for the steel mass rather than to any connection between dissolved gases and the state of oxidation of the inclusion. The development of colored halos surrounding many of the inclusions of a polished steel or Fe section, and of similar rings when such a section is treated with Sb tartrate soln., indicate the correctness of this assumption. Howe's hypothesis with respect to ferrite genesis is regarded as being correct, except for steels during their first cooling from the liquid state. V. O. HOMERBERG

Structure of steels from the standpoint of colloid chemistry. P. C. A. H. LANTSBERRY. *J. Soc. Chem. Ind.* 41, 409-11R(1922).—Cementite is regarded as the dispersed phase and ferrite as the dispersion medium. At high temps. the degree of dispersion is great enough to produce the mol. soln. austenite. As the material cools a temp. is reached at which the dispersed phase assumes the colloidal state and troostite is obtained. Troostite may be regarded as a colloidal soln. in which cementite is the dispersed phase. As the temp. falls the phenomenon of coagulation occurs and sorbite is produced. The examn. of sorbite under the microscope indicates that it has the structure of a suspenoid. On still slower cooling pearlite is obtained and the structure recalls very strongly the phenomenon of periodic pptn. V. O. HOMERBERG

Honda's conception of the A_1 transformation and of the quenching of steel. M. CHIKASHIGE. *Z. anorg. allgem. Chem.* 124, 59-60(1922).—H. has explained the A_1 transformations in steel as a reversible series of products austenite \rightleftharpoons martensite (\rightleftharpoons troostite \rightleftharpoons sorbite) \rightleftharpoons pearlite. The transformation of pearlite into sorbite, troostite or martensite has not been observed. Even though at a temp. slightly below 721°, martensite transforms into austenite, equil. would be difficult to obtain because at such a high temp. austenite rapidly changes to pearlite. F. P. FLAGG

Effect of manganese on carbon steels. H. S. RAWDON AND F. SILLERS, JR. *Iron Age* 110, 1357-61(1922).—102 alloys with the C varying from 0 to 1.60% and Mn from 0 to 2% were used. The effect of Mn as observed in annealed alloys is to confer upon the pearlite a very fine-grained or sorbitic structure, even after slow cooling. The relative amt. of pearlite present is considerably greater in the alloys of high Mn content than corresponding ones low in Mn. A pronounced increase in Brinell hardness of the annealed alloys accompanies the change in structure produced by the addn. of Mn. The addn. of Mn causes a shift in the eutectoid ratio toward lower C content. One % Mn lowers it to approx. 0.78% C. In the normalized alloys, a pronounced decrease in grain size was found in those of higher Mn contents, in addn. to the structural effects mentioned above. In the annealed specimens no noticeable difference in grain size was detected for high and low Mn content in alloys of any given C content. The well known effect of Mn in lowering the transformation temps. of the materials will account in part for the observed structural changes. It appears also that Mn renders steel more "sluggish" and less responsive to structural changes than many of the other elements which produce a similar lowering of the crit. temps. The results strongly support previous recommendations by different metallurgists concerning the advantages of the use of higher Mn, particularly in low- and medium-C steels. V. O. HOMERBERG

Cored structure in quenched manganese steel. S. S. BENJEF. *Chem. Met.*

Eng. 27, 1086(1922).—Photomicrographs are given to show the difference in structure in quenched Mn steel when etched with 3% nital and with LeChatelier's soln. With 3% nital a typical austenitic structure with inclusions of free manganiferous carbide is obtained. A typical dendritic structure is indicated with LeChatelier's reagent. If a photomicrograph is taken of the same specimen after double etching, but without repolishing between nital and the cupric reagent, a close connection is found between the grain boundaries of austenite and dendrites. It is necessary to remove the deposit of Cu by washing with strong NH_4OH before photographing. V. O. HOMERBERG

Problems of corrosion. B. D. SAKLATWALLA. *Ind. Eng. Chem.* **15**, 39-40(1923).—The property of surface tension may play as important a part in corrosion as galvanic action, oxidation, protective films, etc. S. directs attention to a channel of research hitherto neglected from the corrosion standpoint. V. O. HOMERBERG

The corrosion of cast-iron and lead pipes in alkaline soils. J. W. SHIPLEY. *J. Soc. Chem. Ind.* **41**, 311-16T(1922).—The corrosion of cast Fe by soil salts is of the graphitic softening type. Mg salts are the most corrosive of the soil salts, and MgSO_4 is the most effective of the salts tried. Local action induced by naturally occurring concn. cells may easily be a factor in the soil corrosion of cast-Fe pipes. The presence of CaSO_4 in a limy silt soil gives a slight acidity to the ground waters. Auto-corrosion of the cast Fe is promoted by this acidity of the ground waters due to the stimulation provided to the graphite-Fe galvanic couple by the presence of the H ion. Fe more readily displaces H when the latter is present in the ionic condition. The soil corrosion of Fe structures is thus seen to be an electrochem. process, complicated by its dependence upon several variables, of which the compn. of the metal in the structure, the nature of the soil in contact with the metal, and the movements of the ground waters are the most important. Salt solns. attack Pb, a carbonate of Pb being the final product when exposed to the air. Na_2CO_3 was the most corrosive of the salts tried. Pb cathodes are not attacked by currents of from 4 to 10 milliamps. "Coeffs. of corrosion" are not applicable to electrochem. decompn. The presence of NH_4NO_3 appears to inhibit corrosion by the formation of a protective coating of Pb oxide over the surface. Such a protective coating may be only temporary. The soils of the Winnipeg district have a decidedly corrosive action on Pb, the nature of the corrosion being usually that of a crater-like pitting of the surface, with or without an adhering deposit of PbSO_4 or PbCO_3 . Contact with a foreign substance localizes the corrosion. The cause of the corrosion may be attributed to local galvanic action due to differences in the phys. structure of the Pb, to the presence of impurities lodged between the crystals of the Pb, or to concn.-cell effects. V. O. HOMERBERG

The corrosion of iron and steel. T. S. FULLER. *Trans. Am. Soc. Steel Treating* **3**, 94-7(1922).—Corrosion data on iron and steel can quickly be obtained by studying the action of a drop of water on a polished sheet of metal. H_2O and O_2 are necessary for the corrosion of iron. Rusting is best considered as an electrochem. phenomenon. The rate of corrosion depends upon compn., protective measures employed, and the local conditions of surface. W. A. M.

Parkerizing, a combined rust-proofing and finishing process. L. E. ECKELMANN. *Raw Material* **5**, 438-9(1922).—A general description of the method and of its uses.

V. O. HOMERBERG

Protective action of copper in case carburizing. J. C. McCULLOUGH AND H. A. H. PRAY. *Chem. Met. Eng.* **27**, 1119-20(1922).—When soft Fe is heated in a charcoal pack, the CO penetrates into the Fe and gives up some of its C to the Fe to effect the desired carburization. CO gas does not dissolve easily in Cu and hence cannot pass through it unless there are cracks or holes in the Cu. A thin Cu plating over Fe should, therefore, prevent carburization unless there are flaws in the Cu. Such flaws were

found in every plate examd. that had failed to prevent carburization. No breaks were found in the effective platings. V. O. HOMERBERG

Invar, elinvar and other nickel steels. W. D. WILLIAMS. *Raw Material* 5, 330-6, 372-81, 428-37(1922).—A thorough consideration is given to the metallurgy, heat treatment and phys. properties of the high-Ni steels. V. O. H.

Decarburization of ferrochromium by hydrogen. L. JORDAN AND F. E. SWINDELLS. *Bur. Standards, Sci. Papers* No. 448, 327-34(1922); *Chem. Met. Eng.* 27, 1071-2(1922).—To produce rustless iron (a stainless steel in which the C is largely eliminated) a low-C Fe-Cr is needed. The C content of a powd. 8% C Fe-Cr was slowly reduced by dry H at temps. between 1000° and 1350°, temps. at which the alloy is solid. The C is removed much more rapidly by bubbling H through the molten alloy. A sample exposed at 1350° for 4 hrs. lost 1.87% C, while another at 1500-1600° through which H was bubbled lost in 4 min. 0.97%. F. P. FLAGG

Tests on bearing metals. H. A. HOLZ. *Chem. Met. Eng.* 27, 1061-2(1922).—The recommended lab. tests include the microscopic examn. of the alloys, the detn. of the elastic limit under compression, the compressive strength, and hardness. The m. p. of the alloy should be as high as possible. A description is given of a "test bench" for testing bearing metals. The importance of viscosity of a particular lubricant has been overrated. The usefulness of a lubricant depends upon the forces of adhesion to the metal and not upon the cohesion of the oil mols. to one another, i. e., its viscosity. V. O. HOMERBERG

Locomotive brasses and bronzes. HENRY FOWLER. *Metal Ind.* 20, 461-2(1922).—The effect of superheated steam on non-ferrous metals used in locomotives is discussed. V. O. HOMERBERG

Manufacture of brass tubes. W. E. BALLARD. *Iron Age* 110, 1515(1922).—The various defects that arise in the manuf. of brass tubes are considered together with the methods recommended for their correction. V. O. HOMERBERG

Titanium and its commercial alloys. ROBT. J. ANDERSON. *Raw Materials* 5, 440-4(1922).—A careful survey of the progress that has been made in the metallurgy of Ti and in the com. production of Ti alloys is considered. The production of pure metallic Ti by the usual metallurgical reduction processes is exceedingly difficult, owing to the high m. p. of the metal and its strong affinity for N, C, and O. The titaniferous Fe ores, as regards the possibility of their com. utilization, are discussed. One of the most important uses of Ti is for pigments. V. O. HOMERBERG

Insuring permanence in zinc-base die-casting alloys. H. E. BRAUER AND W. M. PEIRCE. *Raw Material* 5, No. 9, 337-40(1922).—The results of a thorough study of the causes and avoidance of failures of the type described by Rosenhain in "Some Failures of Al Alloys" and by Hanson and Gaylor in a "Study of Alloys of Al and Zn" are given. The presence of Pb and Cd in the Zn is detrimental. V. O. H.

Electric arc welding apparatus and equipment. J. CALDWELL. *Electrician* 89, 711-2(1922).—6 illus. C. G. F.

The commercial and technical importance of aluminium (ANON) 4. The role of chemical analysis and of the laboratory in the foundry and in mechanical construction (LEVI) 13.

Hütte—Taschenbuch für Eisenhüttenleute. Compiled by Akademischer Verein Hütte, Berlin. Berlin: Wilhelm Ernst & Sohn. 982 pp. 738 M. Reviewed in *Iron Age* 110, 1505(1922).

Metallurgy of Iron and Steel. (Based mainly on the work of Sir Robt. A. Hadfield.) London & New York: Sir Isaac Pitman & Sons, Ltd. 122 pp. \$0.85.

VITA, A. and MASSENET, C. *Chemische Untersuchungsmethoden für Eisenhütte- und Nebenbetriebe*. 2nd Ed. revised. Berlin: Julius Springer. M 78.

Reducing tin from ores. W. MCA. JOHNSON. U. S. 1,436,961, Nov. 28. Ores contg. Sn and Fe and small amts. of other metals are subjected to a preliminary reduction with H or CO at 600-750° while the withdrawal of gases is regulated so as to permit selective reduction of Sn oxide and the mass is subsequently heated with slag-forming material in an elec. furnace to scorify the Fe and leave nearly pure Sn.

Production of zinc dust. R. B. FINN. U. S. 1,436,983, Nov. 28. Zn is vaporized in a retort and the vapor is condensed in a static body of N.

Removing phosphorus from metal solutions. I. PAUL. U. S. 1,437,191, Nov. 28. An acid soln. is formed (with HCl or H₂SO₄) from refractory metal-bearing material such as ores or compds. of V, U, Cr and Mo and alk. substance, e. g., Na₂CO₃, is added to the soln. to reduce its acidity sufficiently to ppt. siliceous material. The soln. is then treated with alum before pptg. metals in order to hold P in the soln.

Amalgamating metals. R. W. MYERS. U. S. 1,436,518, Nov. 21. An ore pulp is subjected to the action of a heated jet or spray with H₂O heated to 90° so that the jet is directed upon Hg in a receptacle and gives a rotary motion to the contents of the receptacle.

Centrifugal casting of metals. L. CAMEN. U. S. 1,436,305, Nov. 21. A mold is heated to a temp. near the m. p. of Monel metal, steel or other metal to be cast, inserted into a metal sheath to strengthen it and the molten metal is poured into it while the mold is under centrifugal action.

Coating ferrous metals with zinc and antimony. J. SCANLAN and H. GARDNER. U. S. 1,436,729, Nov. 28. Fe or steel is coated with Zn and then with Sb over the Zn coating.

Lead-coated copper sheeting. A. KLEIN. U. S. 1,437,316, Nov. 28. Cu sheeting is "mangled" to produce a rough uneven surface, cleansed with ZnCl₂ soln. and then passed through a Pb bath and treated with H₂SO₄ or a soln. of a chloride or sulfate after cooling.

Ferrotungsten. J. M. SKELLEY and J. MERSON. U. S. 1,437,271, Nov. 28. Ferro-W is formed without use of Al by silico-thermic reduction of Fe and W oxides in the presence of NaNO₃ or Ca(NO₃)₂. U. S. 1,437,272 relates to the similar production of ferro-Mo from Fe and Mo oxides. U. S. 1,437,273 specifies production of ferro-Cr from Fe oxide and Cr or ferro-Cr by silico-thermic reduction in the presence of NaNO₃. Cf. C. A. 17, 54.

Alloy for electrical contacts. F. L. WHITE. U. S. 1,437,844, Nov. 28. Ag is alloyed with U 0.5%.

Welding cast iron or steel. R. MATTICE. U. S. 1,437,257, Nov. 28. An electrode of twisted mild steel strands 85-70 and strands of Cu 15-30% is used for welding cast Fe or steel contg. considerable C.

10—ORGANIC CHEMISTRY

CHAS. A. ROULLER

How organic chemistry should be studied. MAURICE DELACRE. *Mon. sci.* [5] 12, 225-31 (1922).—A philosophical discussion of substitution, valence, and atomic vol., which are the basis of modern conceptions of org. chemistry, showing that these conceptions and the rules derived therefrom should be treated as useful tools but not as scientifically proved theories. A. P.-C.

Mechanism of thermal decomposition of the pentanes. G. CALINGAERT. *J. Am.*

Chem. Soc. 45, 130-5 (1923).—In order to limit the reaction as far as possible to the first stage (formation of H, CH₄ and unsatd. hydrocarbons) and prevent the formation of aromatic compds., the expts. were carried out at the lowest temp. at which the reaction proceeds with a reasonable velocity ($600 \pm 3^\circ$) and the rate of flow of the gas through the hot tube was so adjusted that only a small portion of the pentane was decompd. (30% with $\frac{1}{8}$ g. mol. per hr.). The unsatd. products were detd. quant. by passing the products through Br water and fractionating the resulting bromides, the satd. products by condensing them in liquid air and fractionating *in vacuo*. Pentane (A), gave 44% unsatd. hydrocarbons, or, calcd. on the basis of 44 mols. unsatd. and 56 mols. satd. compds., H₂ 5, CH₄ 12, C₂H₆ 26, C₃H₈ 10, C₄H₁₀ 0, C₅H₁₂ 12, C₇H₁₆ 10, C₈H₁₈ 24, C₉H₂₀ 3, C₁₀H₁₄ 6. These results correspond to a break of the mol. at the central C atom, giving an Et and a Pr group, one of which is satd. at the expense of the other, giving C₂H₆ and C₃H₈ (a) or C₂H₄ and C₃H₆ (b). Considering only that hydrocarbon which is decompd., 55% follows reaction (a) and 25% reaction (b); the largest part of the 20% remaining goes to form a Me and a Bu group; in the latter case it is always the lightest group which becomes satd., giving CH₄ and C₄H₁₀. Isopentane (B) gives 40% unsatd. hydrocarbons or H₂ 6, CH₄ 30, C₂H₆ 24, C₃H₈ 1, C₄H₁₀ 15, C₅H₁₂ 20, C₆H₁₄ 4, C₇H₁₆ and C₈H₁₈ 1. The mol. breaks on one or the other side of the tert. C atom, giving in the first case a Me and an iso-Bu group which, by satn. of the lighter group, yields CH₄ and CH₂:CHEt or MeCH:CHMe, and in the 2nd case an Et and an iso-Pr group, the Et group always being satd., as no C₂H₄ nor C₃H₆ is present. Besides these 2 reactions which utilize 90% of the decompd. B, a small amt. of C₆H₁₀ is formed. Finally, a part of the C₆H₁₄ and C₈H₁₈ formed give, by a secondary reaction, erythrene and isoprene. This last hypothesis was confirmed by treating pure C₆H₁₄ in the same way; the resulting mixt. contained H₂ and CH₄ and 50% unsatd. hydrocarbons, the bromides of which corresponded to those of C₆H₁₄, C₄H₈ and undecompd. C₆H₁₄, showing that the latter itself partly decomp. at 600° with formation of a new break in the chain. Notwithstanding the ease of the reaction and the rapid removal of the decompn. products, no satisfactory yields of unsatd. hydrocarbons of 4 or 5 C atoms were obtained, a fact which seems to leave but little hope that the cracking of the technically valueless petr. ether will provide an easy means for the prepn. of synthetic org. compds. of higher com. value.

C. A. R.

Spontaneous decomposition of unsaturated aliphatic iodochlorides. L. B. HOWELL. *J. Am. Chem. Soc.* 45, 182-7 (1923); cf. *C. A.* 14, 1829.—This paper deals with the decompn. products of the compds. ClCH:CHCl (A), and ICCICCl (B), which, as shown in the 1st paper, decomp. spontaneously and violently in a short time, forming liquid products, with no increase in gas vol. The decompn. of A yields ICl and about 40% CHCl₂CHClI (oil of pleasant odor, darkens slightly on standing with liberation of I, decomp. above 130° under atm. pressure, b_{4-5} 101-2°, d_{20}^{25} 2.266, n_D^{25} 1.5884), 15-20% (CHCl₂)₂ (b_{11} 55.5-6.5°), and less than 10% of a dichlorodiodoethane (heavy oil of pleasant but slightly lachrymating odor, b_{21} 146-8°, d_{20}^{25} 2.861). A in splitting off 2 Cl atoms or a mol. of ICl would leave the residues ClCH-CHI (C) and

ClCH-CHCl (D), resp., which may then be converted into satd. halogen compds. by the 4 possible reactions: C + Cl₂ = CHCl₂CHClI; C + ICl = CHCl₂CHCl₂; D + ICl = CHCl₂CHClI; D + Cl₂ = (CHCl₂)₂. The decompn. of B gives chiefly ICl and (:CClI)₂ (fragrant, pale yellow, highly refractive oil, b_{11} 110.2-0.4°, b 243.4°, m 2.5-3.0°, d_{20}^{30} 2.934), with smaller aints. of *1-chloro-1,2,2-triiodoethylene* (greenish yellow plates from alc., m 77-8°, decomp. unexplosively at higher temps., can be kept unchanged in the dark but turns faintly pink in the light and at once liberates I in direct sunlight), and a const. boiling mixt. (b_{10-2} 66-8°, b_{2-4} 40-1°) of about 80% of the last compd. with

20% of C_2Cl_4 . The formation of the ($:CCl_2$)₂ is accounted for by the splitting off of Cl_2 from B , that of the $CCl_2 : CClH$ by a similar loss of ICl , while to explain the formation of $CCl_2 : Cl_2$ and C_2Cl_4 it is necessary to postulate the replacement of Cl by I in 1 case and that of I by Cl in the other. The only method by which these stable compds. of high and mixed halogen content can be satisfactorily analyzed is the Carius method.

C. A. R.

Preparation of hydroxylamine hydrochloride and acetoxime. W. L. SEMON. *J. Am. Chem. Soc.* **45**, 188-90 (1923).—A soln. of 325 g. dry soda ash in 900 cc. H_2O satd. with SO_2 and cooled in a freezing mixt. is added in the course of 20-30 min. to 410 g. technical (95%) $NaNO_2$ in 1.5 l. H_2O and 1.5 kg. crushed ice (keeping the temp. below 0° by means of ice-salt), treated with SO_2 until acid (the soln. now contains $HON(SO_2Na)_2$), then with 420 cc. technical Me_2CO , heated to 70° to form $Me_2C : NOH$, allowed to cool overnight, and neutralized to litmus with $NaOH$ (1 g. in 2 cc.); the oily layer is removed, the rest of the $Me_2C : NOH$ recovered by distg. the aq. layer with steam and the oil and distillate treated with 450 cc. concd. H_2O . On distn., about 60% of the Me_2CO is recovered and evapn. of the residue on the H_2O bath yields 210-300 g. crude $NH_2OH \cdot HCl$. If $Me_2C : NOH$ is the desired product the oily layer obtained as above is sepd., the aq. layer extd. twice with 100 cc. C_6H_6 and the oxime, b. $133-6^\circ$, sepd. by fractionating the mixt. of oil and C_6H_6 ext.; yield, 280-320 g. The liquid which has been extd. with C_6H_6 always still contains some of the oxime which can be distd. off and treated with HCl , giving 50-60 g. $NH_2OH \cdot HCl$.

C. A. R.

Catalytic dehydration of alcohols in the wet way. I. Olefins and cyclenes. J. B. SENDERENS. *Ann. chim.* **18**, 117-45 (1922).—Olefins and cyclenes were obtained by introducing the catalyst into the alics., the working temp. never exceeding the b. p. of the mixt. C_2H_4 was obtained by heating $EtOH$ (1 vol.) and H_2SO_4 (2 vols.) at 160° , the yield being a max. when 5 g. anhyd. $Al_2(SO_4)_3$ to 100 cc. soln. was employed. F_7O was obtained by heating $EtOH$ (4 vols.) with H_2SO_4 (3 vols. and anhyd. $Al_2(SO_4)_3$ (5 g. to 100 cc. soln.) at $120-30^\circ$. No C_3H_4 was obtained below 140° . The mechanism of the catalysis is: (a) $Al_2(SO_4)_3 + H_2SO_4 + EtOH = H_2O + Al_2(SO_4)_3 \cdot EtHSO_4$; (b) at $120-30^\circ$ $Al_2(SO_4)_3 \cdot EtHSO_4 + F_7OH = F_7O + Al_2(SO_4)_3 \cdot H_2SO_4$; (c) at $150-60^\circ$ $Al_2(SO_4)_3 \cdot EtHSO_4 = C_2H_4 + Al_2(SO_4)_3 \cdot H_2SO_4$. With the higher alics., (c) predominates and no others are formed. Propylene was obtained by heating 100 cc. $PrOH$, 75 cc. H_2SO_4 and 10 g. $Al_2(SO_4)_3$ at $110-30^\circ$. Without the catalyst the temp. required was higher and some hexylene and Pr_2O were formed. Isobutylene was obtained by heating 100 cc. iso-BuOH, 45 cc. H_2SO_4 and 10 g. $Al_2(SO_4)_3$ at 130° . 5% CH_4 and H_2 were obtained as impurities. iso-AmOH gave complex products. iso-PrOH (100 cc.) heated at $102-4^\circ$ with 30 cc. H_2SO_4 gave propylene. With 10% $Al_2(SO_4)_3$ the evolution began at $90-5^\circ$. The use of iso-PrOH is preferable for the production of propylene. Dehydration was attempted, using 4% by vol. of concd. H_2SO_4 at the b. p. of the alc. Catalytic dehydration was noted with tert. alics. (butyl and amyl), with sec. alics. above $PrOH$, and with primary alics. above iso-AmOH. The large excess of H_2SO_4 necessary for the dehydration of the lower members of these series is due to the necessity of raising the b. p. of the mixt. to the point at which catalysis starts. The mechanism of the catalysis by H_2SO_4 is: (a) $H_2SO_4 + C_nH_{2n+1}OH = H_2O + C_nH_{2n+1}HSO_4$; (b) $C_nH_{2n+1}HSO_4 = C_nH_{2n} + H_2SO_4$ (occurs at a temp. at which the acid sulfate is unstable); (c) $C_nH_{2n+1}HSO_4 + C_nH_{2n+1}OH = (C_nH_{2n+1})_2SO_4 + H_2O$; $(C_nH_{2n+1})_2SO_4 = C_nH_{2n} + C_nH_{2n+1}HSO_4$. (c) occurs at a lower temp. at which the acid sulfate is stable. When H_3PO_4 is used in the dehydration of $EtOH$ to give C_2H_4 , it must be heated to $220-30^\circ$ until $H_4P_2O_7$ is formed which then acts as "pivot" for the reaction. Acrolein (34-38 cc.) was obtained by heating 200 cc. glycerol (28° B  ) with 10 g. $KHSO_4$ at 110° for 3 hrs. The action of the bisulfate is: $CH_2(OH)CH(OH)CH_2OH + 2KHSO_4$

$= 2\text{H}_2\text{O} + \text{CH}_3(\text{OH})\text{CH}(\text{SO}_4\text{K})\text{CH}_2\text{SO}_4\text{K} = 2\text{KHSO}_4 + \text{OHCCCH} : \text{CH}_3$. Some $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{KSO}_4$ was formed, which by condensation gave di- and triglycerol resins as residues. K_2SO_4 does not catalyze the reaction as it does not react with glycerol. Tetrahydrobenzene was obtained in 89% yield by heating 100 g. cyclohexanol with 4% by vol. concd. H_2SO_4 . In the same manner *o*-methylcyclohexanol gave Δ^1 - and Δ^3 -methylcyclohexene, the *m*-compd. gave the Δ^2 - and Δ^3 -, and the *p*-compd. gave the Δ^1 -isomer. 2,4-Dimethylcyclohexanol gave Δ^1 - and Δ^4 -tetrahydro-*m*-xylene. Menthol was obtained by distg. menthol with 1-2% by vol. concd. H_2SO_4 . The catalytic dehydration of alcs. in the wet way to give unsatd. hydrocarbons may be accomplished using several catalysts: $\text{Al}_2(\text{SO}_4)_3$, KHSO_4 and H_2SO_4 . This method has the advantage of ease and rapidity, as compared with catalytic dehydration in the dry way (Senderens, C. A. 6, 1607), although the yields are lower and the primary products are less pure.

II. Esters. J. B. SENDERENS AND J. ABOULENC. *Ibid* 145-88.—Esters were obtained by catalytic dehydration of an alc. in the presence of an org. acid. EtOAc in 82% yield was obtained by boiling an equimol. mixt. of AcOH and EtOH with 10 g. of KHSO_4 , the mechanism of the catalysis being: (a) $\text{KHSO}_4 + \text{EtOH} = \text{EtKSO}_4 + \text{H}_2\text{O}$; (b) $\text{EtKSO}_4 + \text{AcOH} = \text{AcOEt} + \text{KHSO}_4$ or (c) $2\text{KHSO}_4 = \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4$. H_2SO_4 (10, 2, or 1% by vol.) acted as a catalyst, giving 86% yields of EtOAc, substantiating (c). However, many esterifications catalyzed by H_2SO_4 are unaffected by KHSO_4 . When the ester formed was volatile the mixt. of the alc. and the org. acids, contg. 2-4% of H_2SO_4 compared to the mol. wt. of the org. acid, was distd. using a Vigreux column. When the ester was difficultly volatile the mixt. was refluxed for 1 hr. Two layers were formed, the upper being the ester, which was sepd. and purified. A series of esters was obtained from monobasic aliphatic acids. The *octanol* or *2-methylhexylcarbinol* esters were obtained by heating the alc. (1 mol.) with the org. acid (1.5 mols.) and 2-3% H_2SO_4 at 100-10°. Dihasic aliphatic acids (malonic, oxalic, succinic) gave a series of esters using H_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, or KHSO_4 as catalyst, the catalytic action of the H_2SO_4 being: $\text{H}_2\text{SO}_4 + \text{ROH} = \text{RHSO}_4 + \text{H}_2\text{O}$; $\text{RHSO}_4 + \text{R}'\text{CO}_2\text{H} = \text{R}'\text{CO}_2\text{R} + \text{H}_2\text{SO}_4$; or for a temp. at which RHSO_4 is stable, $\text{RHSO}_4 + \text{ROH} = \text{R}_2\text{SO}_4 + \text{H}_2\text{O}$; $\text{R}_2\text{SO}_4 + \text{R}'\text{CO}_2\text{H} = \text{R}'\text{CO}_2\text{R} + \text{RHSO}_4$. In the esterification of aromatic acids, when the CO_2H is attached directly to the ring, larger amts. of H_2SO_4 are required and dehydration must be explained by the formation of its hydrates. When the CO_2H is in a side chain, however, the action of the H_2SO_4 is catalytic, analogous to the case of the aliphatic acids. Glycerol esters were obtained by using 1% H_2SO_4 , the action becoming more difficult with acids of high mol. wt. Cyclanols (1 mol.) heated at 100-10° for 1 hr. with aliphatic acids (2 mols.) and 3-4% by vol. H_2SO_4 gave cyclanol esters, no cyclenes being formed at this temp. *Cyclohexanol*, *o*-, *m*-, and *p*-*methylcyclohexanol* and *menthol* esters were prepd., and their b. p., d_4 , and n_D detd. With BzOH and its homologs only cyclenes were obtained. $\text{PhCH}_2\text{CO}_2\text{H}$ and $\text{PhCH}_2\text{CH}_2\text{CO}_2\text{H}$, however, gave cyclanol esters, the consts. for which were detd. H_2SO_4 was found to be preferable to $\text{Al}_2(\text{SO}_4)_3$ and KHSO_4 as catalyst for esterification. The method described gave a rapid and efficient esterification of monobasic and dibasic fatty acids, and aromatic acids by aliphatic alcs. and cyclanols (except when the CO_2H of the aromatic acid is directly attached to the ring).

A. C. PURDY

Simplified method for the resolution of methylhexylcarbinol. JOSEPH KENYON. *J. Chem. Soc.* 121, 2540-2(1922); cf. C. A. 2, 993.—The crystn. of a partly resolved sample of *sec*-octyl-H phthalate (by means of brucine) from AcOH rapidly gives the optically pure forms, these being much less sol. in AcOH than the inactive modification. Details of a typical expt. are given.

C. J. WEST

Quantitative estimation of the Grignard reagent. H. GILMAN, P. D. WILKINSON, W. P. FISCHER AND C. H. MEYERS. *J. Am. Chem. Soc.* 45, 150-8(1923).—Five methods

for the quant. detn. of the Grignard reagent have been studied: (1) Titration with I (Jolibois, *C. A.* 6, 2740); (2) gravimetric method (reaction between PhMgBr and PhNCO); (3) indirect method based on the reactions $\text{RX} + \text{Mg} = \text{RMgX}$ and $2\text{RX} + \text{Mg} = \text{R}_2 + \text{MgX}_2$, the wt. of the reacting Mg being the difference between that taken and that recovered and the wt. of RX reacting being equiv. to that of X distributing itself between RMgX and MgX_2 and detd. by the Volhard method after filtration of the Mg and addn. of dil. HNO_2 to the filtrate; (4) gas analysis (measurement of the gas evolved according to the reaction $\text{RMgX} + \text{H}_2\text{O} = \text{Mg(OH)X} + \text{RH}$; limited to those cases in which RH is a gas); (5) titration with acid, based on the same reaction as (4), the amt. of the basic Mg(OH)X formed, which can be titrated with standard acid, being equiv. to the RMgX originally present. Of these (4) and (5) give satisfactory results. (4) is unquestionably the most accurate of the 5 methods studied. The procedure and the app. used are described in detail. (5) is the simplest of the 5 methods and is not restricted to RMgX compds. having 4 or less C atoms. An apparent disadvantage is its lack of abs. accuracy; the results always run high, but uniformly so. One obvious reason is the almost insurmountable difficulty in prep. absolutely dry reagents and app. and added to this is the fact that a small amt. of moisture decomp. a relatively large amt. of RMgX ; the amt. of acid required for neutralization of the Mg(OH)X will therefore be greater than corresponds to the RMgX actually available. O also decomp. the RMgX , the compd. formed in largest quantity probably being Mg(OR)X , which is likewise basic. Another possible source of error is the acidity which develops in Et_2O on standing (cf. Clover, *C. A.* 16, 1930).

C. A. R.

Optimum condition for the preparation of ethylmagnesium iodide. HENRY GILMAN AND CHARLES H. MEYERS. *J. Am. Chem. Soc.* 45, 159-65(1923).—Using the methods for quant. detg. EtMgI described in the preceding abstr., G. and M. have studied the yields of this compd. under a rather wide variety of conditions. About 9.5 g. EtI in 15 cc. Et_2O (+ 10 cc. Et_2O washings) was added to 1.6 g. Mg under 25 cc. Et_2O in a H atm. The yield of EtMgI (calcd. on the basis of the EtI used) increases steadily with the length of time taken to add the EtI from an av. yield of 85.2% when it is added as rapidly as possible (about 0.5 min.) to a max. of 93.3% when it is added in the course of 45 min. (the mixts. were refluxed for 15 min. after adding the EtI). If no stirring is used, the reaction is slow to start, does not proceed vigorously and gives a very low yield. If, instead of refluxing, the mixt. is stirred for 15 min. after adding the EtI , the yield is increased from 93.3 to 94.4%. A 25% excess of Mg produces an only very slightly improved yield (the increase is within the exptl. error). Diminishing the vol. of Et_2O one-half by adding the EtI (in 25 cc. Et_2O) to the Mg alone decreased the yield from 94.3 to 91.6%. When the mixt. is not protected from the air by a drying tube and the reaction is not carried out in H, the yield is 92.2%. The finer the Mg turnings are, the greater is the yield of EtMgI , but it is the rate of its formation which is the factor really affected. Small amts. of I or PhNM_{22} increase the yield to 95%. Cooling the mixt. in ice during the whole reaction lowers the yield to 84.8%.

C. A. R.

Derivatives of methylstannonic acid; their bearing upon its constitution. HERBERT LAMBOURNE. *J. Chem. Soc.* 121, 2533-40(1922).—It is shown that the so-called methylstannonic acid (A) is not represented by the simple formula MeSnO_2H but is probably a complex mol. contg. 8 atoms Sn. A is best prepd. by slowly stirring 100 g. KOH in 400 cc. H_2O into a freshly prepd. SnCl_2 soln. (42 g. in 100 cc. H_2O); when the ppt. has almost entirely redissolved 30 g. MeI and 250 cc. EtOH are added and the mixt. allowed to stand 3 days. The product is then satd. with CO_2 , the ppt. decompd. by boiling H_2O and washed. Yield, 29 g. Excess of boiling glacial AcOH gives the *pentacetate*, $(\text{AcO})_2\text{MeSn.O.Sn(OAc)Me.O.SnMc(OAc)}_2$, flat prisms, which begins to decomp.

at 250° and on complete ignition leaves a residue of SnO. Excess of H₂O hydrolyzed this to A and AcOH. Small amts. of H₂O and EtOH gave the *triacetate*, (AcO)MeSn.O.Sn(OAc)Me.O.SnMe(OAc).O, also obtained by the action

of a small quantity of glacial AcOH on A, rhomboids, decomp. about 280°. Prolonged boiling with AcOH gave the pentaacetate, while H₂O completely hydrolyzed the substance. *Pentachloroacetate*, minute rhombohedrons, m. 214–24° (decompn.). *Pentafornate*, fine needles, decomp. between 240–80°, readily sol. in H₂O and completely hydrolyzed by boiling. Partial hydrolysis with EtOH gave the *triformate*, rhomboids, decomp. 270°. Prolonged boiling caused further hydrolysis. It is insol. in H₂O and most org. solvents. The *pentabenzoate*, obtained by the action of fused BzOH upon the pentaacetate, or by adding A to the fused acid, the excess BzOH being removed with Et₂O, minute rhombohedrons, m. 272°. It is insol. in H₂O but readily sol. in EtOH. The triacetate appears to be very similar to A in constitution and this is taken as evidence of the termol. structure of the latter. C. J. WEST

9,11-Decylenic acid, a hitherto unknown acid from butter. AD. GRÜN AND TH. WIRTH. Ber. 55B, 2197–2205 (1922).—Hitherto, there was known no well authenticated case of the existence in any fat of an *unsatd.* acid with less than 16 C atoms. G. and W. worked up 550 kg. butter and using the fraction of the acids b₁ 100–40° have been able to obtain about 40 g. of *9,11-decylenic acid* (A), CH₂:CH(CH₂)₈CO₂H. Undoubtedly the other fractions contain more of this acid and also other acids of the same kind and the isolation is also without doubt far from complete. In the course of the isolation there was finally obtained a mixt. which, from at. grouping detns. and degradation expts., consisted of approx. equimol. amts. of A and capric acid and which could be sep'd. no further by any of the known methods, but by converting the mixt. into the Me esters and brominating it became possible to sep. the resulting higher boiling Br deriv. of A from the unchanged Me caprate by fractional distn. The *methyl dibromocaprate* b₁ 185–6° and with HCl and Zn in boiling MeOH gives the *methyl ester* of A, mobile oil of faint but characteristic pleasant odor, b₁₂ 115–6°. The free A m. below 0°, b₄ 142°, is identical with the synthetic product (see following abstr.); on long standing the I and neutralization uos. (originally 142.4 and 330.8, resp.) decrease proportionately in about the ratio 1:2 and the odor of decalactone gradually develops. Ozonization of the Me ester in CHCl₃ and subsequent decompn. of the ozonide with H₂O gives formic and azelaic acids. C. A. R.

Synthesis of 9,11-decylenic acid. AD. GRÜN AND TH. WIRTH. Ber. 55B, 2206–18 (1922); cf. preceding abstr.—CH₂:CH(CH₂)₈CO₂Me (A) is obtained in 4050 g. yield from 9400 g. Me ricinolate dropped at the rate of 150–200 g. per hr. into a quartz flask at 250°, the vapors of A, enanthole and unchanged ricinolate being drawn through a hot quartz tube. The Et ester is similarly obtained; 100 g. of this (dried several days over K₂CO₃) in 500 cc. slightly warmed abs. alc. treated in the course of 10 min. with 50 g. Na, allowed to react 0.5 hr. longer with vigorous turhining, poured into warm H₂O and freed from the alc. by distn. gives practically quant. *1-undecen-11-ol* (B), b. 250°, b₃ 122°, solidifies –7° to frost-like leaflets; 50 g. in 100 cc. Et₂O in ice-salt treated in a current of CO₂, in the course of 20–30 min., with 35 g. ClSO₃H, treated 1 hr. longer with CO₂, poured into 2 vols. ice water, neutralized with K₂CO₃, freed from unchanged B and a little chloroundecene (together about 4 g.) with Et₂O and from Et₂O by heating and treated with an excess of hot BaCl₂ gives about 50 g. of the *barium salt*, (C₁₁H₂₁OSO₄)₂Ba, leaflets, of *undecenylsulfuric acid* (C) which in boiling H₂O splits off H₂SO₄. The acetate of B with CrO₃ in boiling AcOH gives 35–41% of its wt., with KMnO₄ or Ca(MnO₄)₂ about 72% of *1-acetoxycapric acid* (D), b₁₃ 213°, loses AcOH at 320°; *methyl ester*, almost odorless, b₁ 175°, b₁₆ 163°, b. 295–300° practically unchanged, slowly decomp. on long heating, splitting off AcOH, which in turn hydrolyzes

the ester to AcOMe ; *amyl ester*, $b_p 210^\circ$, $b_r 310-2^\circ$ (slight decompn.). The crude **D** boiled with HCl in MeOH gives AcOMe and the *methyl ester*, $b_p 154^\circ$, solidifies 34.5° , of *4-hydroxycaproic acid* (**E**), $m. 75^\circ$, loses H_2O on heating with formation of an inner ester; *amyl ester*, prep'd. from AmOH ($b_p 131^\circ$), $b_r 179-80^\circ$. The oxidation of **C** is cheaper, more convenient and gives an even better yield than that of the acetate. The **C** need not be isolated; 50 g. **B** treated as above with 25 cc. ClSO_3H , freed from the Et_2O , dissolved in 1 l. H_2O , treated in the course of 1 hr. below 50° with 160-70 g. powdered KMnO_4 , filtered when the purple color persists for 0.5 hr., decolorized with NaHSO_4 , neutralized with KOH , concd. to 250 cc., treated with an equal vol. of HCl , boiled 15-30 min., sepd. from the aq. acid layer, boiled with alc. KOH to decomp. the inner ester, freed from unchanged **B** and the undecanetriol (about 2-5 g. together) with Et_2O and pptd. with acid, gives 30-8 g. **E**. *Methyl 4-chlorocaproate*, from the Me ester of **E** and PCl_5 in ice-cold CHCl_3 , $b_p 153^\circ$; boiling concd. KOH quant. removes the Cl in 1 hr. but gives chiefly **E** and not the desired δ,ω -decylenic acid (**F**); PhNI_2 is not sufficiently strong; 5 vols. quinoline quant. eliminates the Cl after 2 hrs. reducing but the desired formation of **F** is only partially effected, the I no. of the product being only 61. Attempts were then made to synthesize **F** by destructive distn. of the acyl derivs. of **E**. The Me ester of **D** proved too stable; the Am ester also gives only about $1/2$ the calcd. amt. of olefin deriv.; the free **D** gives off AcOH abundantly, to be sure, on distn. but besides the **F** there are formed inner esters of **E**. When, however, *methyl 4-stearoyloxycaproate*, from the Me ester of **E** heated on the H_2O bath in a current of CO_2 with 1.5 parts stearyl chloride, soft, waxy, spherical aggregates from MeOH , $m. 43^\circ$, is distd. up to 340° , the distillate is hydrolyzed and acidified, the resulting acids are freed from most of the stearic acid and the unchanged **E** by fractional crystn. from petr. ether and the petr. ether-sol. fraction is sepd. by the bromination method described in the preceding abstr., about 100 g. of the Me ester of **F** is obtained from 250 g. **E**. **F** was also synthesized with sebacic acid as the starting point. Di- Me sebacate, needles from Et_2O , long thick prisms from the melt, $m. 27-8^\circ$ (given in the literature as $26-8^\circ$); *diethyl ester*, liquid of a very delicate pleasant odor, $b_p 172^\circ$. Systematic exps. to det. the optimum conditions for partial sapon. to the monoalkyl esters proved of little practical value. Skillful technic in mixing the alkali and ester solns. is the most important factor. The solns. must be as concd. as possible. The ester in 0.5 vol. alc. is allowed to react a few sec. with the calcd. amt. of at least 2 N warm alc. KOH , the resulting magma is dissolved in ice H_2O , the unchanged neutral ester extd. with Et_2O , the aq. soln. acidified, and the free sebacic acid and the acid ester extd. with Et_2O and fractionated from low boiling petr. ether. *Monoethyl sebacate* (yield, 40-50%), $m. 36^\circ$, $b_p 210^\circ$, rearranges into the free acid and the di- Et ester on distn. under atm. pressure. It is best reduced in the form of its K salt (prep'd. by neutralizing in MeOH with KOH , evapd. and drying over P_2O_5), which, slowly treated in boiling alc. with Na , dild. with H_2O till a clear soln. results, freed from 0.5 of the alc. by distn., acidified, extd. with Et_2O , evapd., boiled with Ac_2O to convert the product into **D**, then boiled with MeOH and sapond. gives 43-56% **F**. In the preceding abstr. it was stated that on standing the I and acid nos. of **F** decrease proportionately, indicating an intramol. reaction (addn. of the CO_2H group at the double bond with formation of a lactone or estolide). Undecylenic acid, the next higher homolog of **F**, gives, with moderately dil. H_2SO_4 , a γ -lactone formed by migration of the double bond or the HO group of the intermediate HO acid (Zhukov and Shestakov, *C. A.* 3, 1148). **F**, stirred 8 hrs. with an equal wt. of 80% H_2SO_4 , gives 80% of *decalactone*, $\text{C}_{10}\text{H}_{18}\text{O}_2$, $b_p 153^\circ$, is satd. (adds only traces of ClI), reacts neutral, is only slightly decompd. even by HCl in MeOH , hydrolyzed by alc. KOH to the free acid, fine leaflets from gasoline, $m. 44^\circ$, which is odorless but soon develops the odor of the lactone and after several weeks completely changes into a mixt.

of the lactone and H_2O . Z. and S.'s undecalactone, b, 173–4°, was obtained in 60% yield and quant. converted into the hydroxyundecanic acid, scales from Et_4O -petr. ether, m. 49–50° (Z. and S. give 34°); oxidation with CrO_3 gave a ketonic acid, fine needles, m. 178°, whose semicarbazone m. 122°.

C. A. R.

Oxidation of propyleneglycol with potassium permanganate. W. L. EVANS. *J. Am. Chem. Soc.* **45**, 171–6(1923); cf. *C. A.* **6**, 3089; 17, 57.—Propyleneglycol is oxidized by neutral $KMnO_4$ at 50° and 75° to $AcOH$ and CO_2 ; above certain min. concns. of alkali, $(CO_2H)_2$ is also formed. Lactic (A) and pyruvic acids (B) are probably 2 of the intermediate compds. in these oxidations. The A is produced either by the oxidation of $MeCH(OH)CHO$ or the rearrangement of $AcCHO$ in the presence of acids. The B is an oxidation product of A. The $AcOH$ in these oxidations is probably formed by the oxidation of AcH , present as a dissociation product, and of B. The $(CO_2H)_2$ is probably formed by oxidation of glycolic acid, resulting from the oxidation of $CH_2 : CHOH$, and of glyoxylic acid formed from B by the successive formation of dihydroxypruvic and formylglyoxylic acid. CO_2 is probably formed by the oxidation of $HCHO$, of B and of glyoxylic acid, which in neutral and very weakly alk. solns. is converted exclusively into CO_2 . Increase in temp. increases the yield of CO_2 and diminishes that of $AcOH$. The alkali functions by neutralizing the acids formed, increasing the enolization of AcH and causing the rearrangement of $AcCHO$ to A. As the concn. of the alkali is increased the dissociation of the 3-C atom compds. into 2 other compds. is suppressed in that direction, owing to the increased reactivity of the alc. groups in the glycol resulting from the lower point of dissociation of the alcoholates formed in comparison with that of the glycol itself.

C. A. R.

Synthesis of glycine from formaldehyde. A. R. LING AND D. R. NANJL. *Biochem. J.* **16**, 702–3(1922).—The method of preparing glycine is a modification of Klages' method (*Ber.*, **36**, 1508(1903)), which is based on the reaction between 2 mols. $HCHO$ and NH_4CN , giving $CH_2 : NCH_2CN + 2H_2O$. Instead of hydrolyzing the nitrile with HCl (Klages' method), which makes it difficult to sep. the glycine from NH_4Cl , L. and N. use 40% $Ba(OH)_2$.

BENJAMIN HARROW

The thiocarbamide reaction. SHINTARO KODAMA. *Japan. J. Chem.* **1**, 81–93 (1922).—An English translation of the paper abstracted from the Japanese in *C. A.* **15**, 1511.

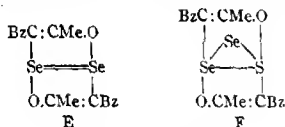
K. K.

Decomposition of dithiocarbazates. SIMA M. LOSANYTCH. *J. Chem. Soc.* **121**, 2542–5(1922); cf. *C. A.* **15**, 2829.—Dithiocarbazinic thioanhydride (A), $(NH_2NHC)_2S$, or the isomeric form $(HSC : NNH_2)_2S$, is obtained together with S, when an aq. or alc. soln. of an NH_4 or substituted NH_4 dithiocarbamate is evapd. to dryness; it forms small plates or needles from alc., which change at 170° and m. 225°. With MeI it yields the di-Me ether (Zeigle, *J. prakt. Chem.* **60**, 42) of 2,5-dithio-1,3,4-thiadiazole (B) (Busch, *Ber.* **27**, 2518), which is most conveniently prepd. by the action of CS_2 on $N_2H_4 \cdot H_2O$ in alc. NH_3 . B. is inclined to regard A as the hydrazine salt of B, although the acid can be set free only by concd. HCl . When B in H_2O or alc. is boiled for several days, 2-thiol-1,3,4-thiadiazolyl monosulfide is formed, faintly yellow needles, decomp. 178°; the alkali and NH_4 salts are sol. in H_2O , those of the heavy metals, insol. The Ag and Ph salts are yellow, the Cu salt is brown and the Co salt green. The dimethyl ether m. 71°. In addition to the disulfide prepd. by Z., a cryst. yellow polysulfide, m. 186°, is also formed, which is insol. in $EtOH$. It probably has the structure $S.(HN : C)S.C.(: NH).S.S.C.(: NH).S.S.$

C. J. WEST

Residual affinity and coördination. IX. Interaction of selenium tetrachloride and β -diketones. G. T. MORGAN, H. D. K. DREW AND T. V. BARKER. *J. Chem. Soc.* **121**, 2432–73(1922); cf. *C. A.* **16**, 2479.—Se acetyl acetone(A) is conveniently prepd. by adding 25 g. powdered Cu deriv. during 15 min. to 20.5 g. $SeCl_4$ suspended in 120 cc.

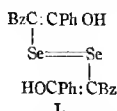
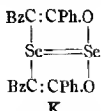
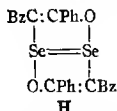
pure CHCl_3 ; after 30 min., the CuCl_2 is removed and the CHCl_3 soln. evapd. in a stream of air. A is not affected by MeI , EtI , AcMe or MeCN . HCl in dry Et_2O dissolved A but did not further change it. Aq. HCl formed an unstable addn. compd., sol. in Et_2O . NH_3 decompd. A completely in a sealed tube, giving Se , AcNH_2 and HCN . A crysts. in 2 distinct modifications, the 1st of which is orthorhombic, the 2nd monoclinic. The 2nd form may be transformed into the 1st by crystn. from C_6H_6 . *Diselenium bisacetylacetonate*, $[\text{AcC}(\text{CMeOH})\text{Se}]_2$ (B) was prepd.: from SeCl_4 and the Cu deriv. in CHCl_3 at 0° ; by adding powdered A to a cooled mixt. of Et_2O , HI and H_2O ; and from SeCl_4 and the Cu deriv. The HI method gives the best yield. From light petroleum, B crysts. in bright orange 6-sided plates or prisms having a fatinnaceous and burnt-rubber odor, nearly lost on drying. Usually it softened at 78° and m. $92\text{--}3^\circ$, but some samples softened at 58° and m. $78\text{--}80^\circ$. The system is orthorhombic, $a : b : c = 0.954 : 1 : 1.727$, the forms developed being $c(001)$, $q(011)$, $b(010)$ and $r(101)$. B is isomorphous with the corresponding dithio compd. In warm alc., B decomp. into red Se , acetylacetonate (C) and a yellow oil. Dry NH_3 gives a yellow ppt. (NH_4 salt?), easily decompd. by atm. moisture. 5 N NaOH rapidly dissolved the compd., liberating Se . $\text{N}_2\text{H}_4\cdot\text{HCl}$ and PhNHNH_2 liberated Se in AcOH and EtOH , resp. FeCl_3 gives an intense red color. The copper salt is yellow, sparingly sol. in C_6H_6 or CHCl_3 , reddens at $130\text{--}5^\circ$ and decomp. $150\text{--}70^\circ$; 5 N NaOH dissolves it with a yellow color, changing to red and then black. The reaction of A with HCN is one of addn. and depolymerization; the product, *cyano-3-selenium acetylacetonate*, $\text{CNSeC}(\text{OH}) : \text{CMe}(\text{OH})$, forms brittle needles, m. $78\text{--}80^\circ$; it is highly sternutatory and in the light and air became brownish pink and gave off HCN ; KHSO_4 decomp. it into C, HCN and $\text{Se}(\text{SO}_3\text{K})_2$. The enolic



character is manifested by the red color with FeCl_3 and the formation of a *copper derivative*, light blue, very slightly sol. in boiling CHCl_3 and decompd. by AcOH or NaOH . *Selenium O,C-bisacetylacetonate* (D), $\text{HOCMe} : \text{CAcSeOCMe} : \text{CHAc}$, is produced by heating 1 part A with 3 parts C in 6 parts Et_2OH , or by shaking SeCl_4 and the Cu deriv. in dry CHCl_3 ; it crysts. in enantiomorphous forms of the monoclinic system, with $a : b : c = 0.8872 : 1 : 1.107$, $\beta = 110^\circ 55'$. The forms observed on a right-handed crystal were $a(100)$, $c(001)$, $r(\bar{1}01)$, $m(1\bar{1}0)$, $m'(\bar{1}\bar{1}0)$ and $q(011)$. Rapidly heated, D m. $50\text{--}54^\circ$; slowly heated, it softens at 42° , because of dissociation, which also occurs in hot EtOH , MeOH , H_2O and partly in MeCN . In aq. NaOH the yellow soln. turned to red, liberating Se ; this occurs more slowly in NaHCO_3 . Dry NH_3 in Et_2O ppts. a yellow, unstable NH_4 salt. FeCl_3 gives a deep red color. The reaction with aq. KHSO_4 occurs in 2 stages. *Copper salt*, sage-green, slowly decompd. by boiling CHCl_3 . *Selenium C-ethyl-O,C-bisacetylacetonate*, $\text{HOCMe} : \text{CAcSeOCMe} : \text{CEtAc}$, short, rod-like needles or compact prisms, softens $65\text{--}7^\circ$, m. $77\text{--}82^\circ$. This gives an intense red color with FeCl_3 , a pale blue *copper salt* and is dissociated by warming with H_2O or EtOH . The reaction of A with MeSH in Et_2O gave an oil; this developed an intense red color with FeCl_3 and gave a yellowish green *copper salt*, small, green crystals, decomp. $164\text{--}7^\circ$. The reaction with $\alpha\text{-C}_{10}\text{H}_7\text{SH}$ gave B and $\alpha\text{-naphthylthioselenium acetylacetonate}$, bright cowslip-yellow crystals, m. $81\text{--}3^\circ$; this gives a red color with FeCl_3 and a greenish yellow *copper salt*. The reaction between $(\text{BzCH} : \text{CMeO})_2\text{Cu}$ and SeCl_4 takes place in 2 ways, 2 or 3 mols. of each reacting together. In the 1st instance the reaction product is *selenium benzoylacetonate* (E), small, pale primrose-yellow, 6-sided plates, existing in

2 closely related varieties, 1 becoming discolored at 175° and decomp. at 200°, the other not changing color below 207° and m. 210-2°. In the 2nd instance, the reaction product is *cyclotriselenium bisbenzoylacetone* (F), sepd. from E by its greater soly. in CHCl_3 , which forms small, prismatic, bright yellow monoclinic crystals, decomp. 196-200°. It is readily decompd. by hot HCl ; it has no enolic properties. HI decomp. it into Se and E, I being liberated. *Cyano-3-selenium benzoylacetone*, transparent needles, m. 70°; FeCl_3 gives an intense red color. $\text{Cu}(\text{OAc})_2$ gives a greenish blue *copper salt*, m. 131°. The compd. is very sensitive to light, Se being eliminated. The mother liquors from E and F gave *3-chlorobenzoylacetone*, needles, m. 40-3°; it possesses a pungent lachrymatory odor and a considerable vapor pressure at the ordinary temp. It gave a red color with FeCl_3 and a light green *copper salt*. With $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHNH}_2$ in abs. alc., it gave *4-chloro-5(or 3)-phenyl-1-p-nitrophenyl-3-(or 5)-methylpyrazole*, pale orange needles or elongated plates, m. 156-8°. The Cu salts of diketones may be transformed into halogenated derivs. by the action of Cl in CHCl_3 . This method is probably capable of considerable extension. *Diselenium bisbenzoylacetone*, prepd. by the action of HI upon Se benzoylacetone (G) or F, bright orange, 6-sided prisms, orthorhombic, isomorphous with the corresponding dithio deriv., $a : b : c = 0.734 : 1 : 0.4110$, $b(010)$, $a(100)$, $c(111)$, $r(101)$. FeCl_3 gives a violet-red color and $\text{Cu}(\text{OAc})_2$ a brownish yellow *copper salt*. PhNHNH_2 in EtOH liberates Se, especially on warming. *Selenium O,C-bisbenzoylacetone*, $\text{BzCH} : \text{CMcOSeCHBzAc}$, by the action of 1 g. G upon 3 g. BzCH_2Ac in CHCl_3 contg. a trace of solid NaOH, microprisms, m. 134-6°; this does not give a Cu salt and very slowly developed a red color with FeCl_3 . It is dissociated by boiling with any moist solvent. The addn. of a trace of solid NaOH to a suspension of G in C or of A in BzCH_2Ac caused complete soln., from which A or G could be isolated; i. e., G may be transformed into A and *vice versa*. The action of SeCl_4 upon Ac_2CHEt in Et_2O gave only Se and the 3-Cl deriv. With the Cu salt, 2 definite compds. were isolated. 2 mols. Cu salt to 1 mol. SeCl_4 in dry CHCl_3 gave *selenium bis-C-ethylacetylacetone*, $\text{Se}(\text{CETAc})_2$, transparent 6-sided prisms or needles from alc., m. 81-2° and liberating Se at about 200°. It is non-enolic. It is slowly decompd. by 5 N NaOH, forming MeCOPr(?) , and also by warm concd. HCl and Br. The constitution is established by the quant. decompn. by 50% HI into Ac_2CHIEt and Se. When 2 mols. SeCl_4 are used the product is the *diselenium compound* $(\text{Ac}_2\text{EtCSe})_2$, lemon-yellow, 6-sided needles or prisms, m. 117-8°, decomp. 210°. It resembles the mono-Se deriv. in its reactions, except that it is decompd. by KHSO_4 into Ac_2CHIEt and Se. The action of SeCl_4 upon Bz_2CH_2 or its Cu deriv. gave *chlorodibenzoylmethane*, needles, with a mixed aromatic lachrymatory odor, m. 87-8°. It is not markedly enolic. *Selenium bisbenzoylmethane*, $\text{Se}(\text{CHBz})_2$, is obtained by the action of 3 mols. SeCl_4 upon 4 mols. of the Cu salt, large, yellowish white, 6-sided monoclinic prisms, m. 150-2°; $a : b : c = 1.07 : 1 : 0.75$, $\beta = 91.5^\circ$; $a(100)$, $m(110)$, $c(001)$, $r(101)$, $R(\bar{1}01)$. From C_6H_6 , the compd. crysts. with 1 C_6H_6 as microneedles. This compd. is comparatively inert. *Selenium dibenzoylmethane* (H), lustrous, pale golden yellow plates with 2 C_6H_6 , m. 211° with liberation of Se. A by-product of the reaction, sol. in AcOEt , is *cyclotriselenium bisdibenzoylmethane* (I), $\text{Se}_3(\text{C}_6\text{H}_5\text{O})_2$, pale orange-yellow, m. 220°. The action of HI upon I or H in $\text{Et}_2\text{O}-\text{CHCl}_3$ gave *diselenium bisdibenzoylmethane* (J), felted masses of slender, orange-yellow prismatic needles, m. 116-8°. It gives a red color with FeCl_3 and an olive-green *copper salt*, sol. in CHCl_3 . *Cyanoselenium dibenzoylmethane*, prismatic needles, m. 100-1°; it gives a blood red color with FeCl_3 but does not yield a Cu deriv. When H is heated 0.5 hr. at 135-40°, some Bz_2CH_2 is eliminated and *isoselenium dibenzoylmethane* (K) is formed; this forms rosetts of pale golden yellow needles or flakes, m. 175-6°. When H or K is heated at 160-85° for some time, *selenium dehydrobisbenzoylmethane* (L) results, also formed by the action of HCN or HI upon K, small,

refractive, bright orange monoclinic crystals, m. $190-1^{\circ}$, $a : b : c = 2.10 : 1 : 1.49$, $\beta = 99^{\circ}$; $c(001)$, $a(100)$, $x(310)$, $o(111)$, $p(\bar{1}11)$. It shows no acidic or enolic properties;



it is not affected by boiling HCl, alkali bisulfites, $\text{Et}_3\text{O-HI}$ or $\text{H}_2\text{O-HCN}$. Warm KOH decomps. it, forming Se and PhCOMe. Reduction with Na-Hg gave Se, PhCOMe, Bz_2CH_2 and BzH. L was also produced by the action of $\text{Et}_3\text{O-HI}$ or HCN upon K.

C. J. WEST

Experiments in the field of keto-enol tautomerism (preliminary communication).

H. P. KAUFMANN. *Ber.* 55B, 2255-7(1922).—*Cl. C. A.* 17, 379.

C. A. R.

Electrosynthesis of azelaic and thapsic acids. MABEL CARMICHAEL. *J. Chem. Soc.* 121, 2545-9(1922).—Although the constitution of azelaic (A) and thapsic (B) acids has been established chemically, it was thought desirable to synthesize these acids electrolytically. A and suberic acid (C) were prepd. from castor oil, the best yield being obtained by first hydrolyzing the oil and then oxidizing the acids. The 2 acids were sepd. by the greater soly. of A in H_2O . C was converted into the KEt ester and a 50% aq. soln., mixed with 50% aq. $\text{K}_2\text{C}_2\text{H}_3\text{O}_2\text{Et}$, in the proportions of 1 : 3, was electrolyzed in a Pt crucible, which acted as cathode; the current averaged 1.7 amp. with a voltage of 7.5; the temp. was 15° . After 2 hrs. 4 cc. pale oil were obtained from 20 cc. soln. The mixt. of acids resulting from the sapon. of the esters was sepd. by hot H_2O , the $(\text{CH}_2)_{11}(\text{CO}_2\text{H})_2$ being insol., while A crystd. out on cooling and $(\text{CH}_2\text{CO}_2\text{H})_2$ remained in soln. In the same way, the electrolysis of A gave an acid identical with thapsic acid, m. 124° . A by-product of this synthesis is *ethyl n-heptenecarboxylate*, b. 210° .

C. J. WEST

Alkylglycerols; conversion of vinylalkylcarbinols into alkylglycerols. RAYMOND DELABY. *Compt. rend.* 175, 1152-4(1922).—The second step (*Compt. rend.* 175, 967 (1922)) in the prepn. of alkylglycerols (A) involves the addn. of Br_2 to the vinylalkylcarbinol (B) and the transformation of the dibromohydrins thus formed into diacetins by means of KOAc in AcOH. Br_2 is added to the ethylenic alc. in 3 times its wt. of AcOH, and the mixt. cooled in ice and NaCl. After 12-24 hrs. the theoretical amt. of KOAc, recently melted and pulverized, is added, and then the mixt. is refluxed on the oil bath during 15-20 hrs., agitating continuously. The reaction product is distd. *in vacuo*, the AcOH coming over first and then the acetin passes over. $\text{MeC}_3\text{H}_7(\text{OAc})_2$, $b_{12} 142-5^{\circ}$, $b_{27} 153-5^{\circ}$ (Lieben and Zeisel, *Monatsh.* 1, 832(1880)); $\text{EtC}_3\text{H}_7(\text{OAc})_2$, $b_{21} 156-8^{\circ}$, $b_{32} 264 5^{\circ}$ (Wagner, *Ber.* 21, 3349(1888)); *propylglycerol triacetate*, $b_{15} 157-9^{\circ}$; *butylglycerol triacetate*, $b_{21} 174^{\circ}$. The sapon. of the acetates (C) was not effected with alkalis to the end that compds. of a glycidic structure and condensation of the A should be avoided. Hydrolysis by means of H_2O under 2 atms. pressure, and of MeOH and by means of a mixt. of these reagents could not be effected. C is heated at 98° in MeOH contg. 10 g. HCl per l. in the ratio of 6 moles for every mole of B. The AcOMe and MeOH are distd. and the B is then distd. *in vacuo*. Small amts. of C are sapon. by $\text{Ca}(\text{OH})_2$. C in 3-6 times its wt. of H_2O is mixed with a little more than the calcd. amt. of $\text{Ca}(\text{OH})_2$ and the operation is conducted in an autoclave under 2 atms. pressure for 2 hrs. The excess of $\text{Ca}(\text{OH})_2$ is removed by CO_2 . After boiling the mixt., cooling and filtering, the product is distd. *in vacuo*. $\text{MeC}_3\text{H}_7(\text{OH})_3$, $b_{15} 162.5-3.5^{\circ}$, $b_{27} 172-5^{\circ}$ (L. and Z.); $\text{EtC}_3\text{H}_7(\text{OH})_3$, $b_{15} 165-6^{\circ}$, $b_{23} 192^{\circ}$ (W.). *Propylglycerol* (D) $b_{14} 167.5-68^{\circ}$; *butylglycerol* (E) $b_{17} 175-5.5^{\circ}$. All of these compds. are very hygroscopic, of bitter taste; D and E are cryst.; by rapid warming on a Hg bath D m. $60-2^{\circ}$ and E

m. 52-4°. Wagner employed a KMnO_4 oxidation of **B** in prep. $\text{EtC}_4\text{H}_9(\text{OH})_2$, using very dil. solns. Other oxidation products were formed simultaneously, as well as hydration products. The method proposed by **D**. can be used for large-scale production. The yields are 60% and large quantities of H_2O are avoided. H. E. WILLIAMS

Purines. IV. Action of hydrogen peroxide upon certain phenyl-substituted uric acids. F. J. MOORE AND ELIZABETH S. GATEWOOD. *J. Am. Chem. Soc.* **45**, 135-45 (1923); cf. *C. A.* **12**, 1782.—It was shown in the earlier papers that H_2O_2 , acting upon uric acid (**A**) in a soln. whose alk. is less than 1 *N* and temp. higher than 80° gives allantoin and carbonyldiurea, the latter in a soln. more strongly alk. than 0.5 *N* being converted into cyanuric acid (**B**); on the other hand, at room temp. and in soln. more strongly alk. than 1 *N*, the product is allantoxanic acid, which, if the soln. is acidified before removing the H_2O_2 , is oxidized to **B**. No intermediate product between the **A** and the above products was found, however, and no light was thrown upon any relationship which may exist between the mechanism of this reaction and the KMnO_4 oxidation. Accordingly, the action of H_2O_2 upon numerous purine derivs. (theobromine, caffeine, xanthine, guanine, 3-, 7- and 9-methyl- and 7-oxymethyleneuric acids, and 3,7-dimethyl-4,5-uric acid glycol) was studied but all the results were negative in the sense that they did not invite further study; some of the compds. were unaffected, some were decompd. by the alkali; still others gave jelly-like mixts. 9-Phenyluric acid (**C**), however, finally gave homogeneous products in reasonable yields, viz., NH_3 , $(\text{CO}_2\text{H})_2$, PhNHCONH_2 , asym-phenylbiuret (**D**) and a compd. (**E**) which is converted into **D** by NH_3 and proved to be a new phenylbiuret entirely distinct from the 2 already known (see below). On the other hand, 1,3-dimethyl-*g*-phenyluric acid (**F**) and 7-methyl-*g*-phenyluric acid (**G**) yield no substituted biurets but NH_3 , $(\text{CO}_2\text{H})_2$ and PhNHCONHMe (**H**). Assuming that **E** is the true sym-phenylbiuret, $\text{PhN}(\text{CONH}_2)_2$, and since **D** is probably formed only by the transformation of **E**, the oxidations of **C**, **G** and **F** can be interpreted from a single point of view; the 1st step is regarded as consisting in the breaking of the bonds between positions 2 and 3, 4 and 5, and 5 and 7, giving **E** in the 1st case and in the other two the same $\text{H}_2\text{NCONPhCONHMe}$ which decomps. into NH_3 , CO_2 and **H**, while the **E** partly undergoes a similar decompn. into PhNHCONH_2 and another part is rearranged by the NH_3 into **D**. Not too much is claimed for this interpretation; its weakest point is the fact that **E** on similar treatment gives no PhNHCONH_2 , which may, therefore, come from some other source. This, however, does not necessarily invalidate the other assumptions. This question cannot be definitely settled until the aryl substituted biurets have been thoroughly studied. 7-Methyl-*g*-phenylpseudoauric acid (7 g. from 5 g. of 7-methyluramil in 60 cc. of *N* KOH at 0° treated with 5 g. PhNCS in small portions), needles, m. 245-50° to a yellow liquid, shows parallel extinction, α 1.636, γ 1.714+; 3 g. boiled with 600 cc. of 35% HCl and concd. gives 76% of **G**, needles, does not m. 265°, gives the murexide reaction, extinction parallel, α 1.557, γ 1.674+. 1,3-Dimethyl-*g*-phenylpseudoauric acid, obtained in 28-37 g. yield from 30 g. 1,3-dimethyluramil in 360 cc. of *N* KOH treated below 4° in the course of 1 hr. with 30 g. PhNCS , or in 5 g. yield from 5 g. of 9-phenylpseudoauric acid in 40 cc. of 2 *N* KOH shaken 1 hr. at 0° with 11 g. Me_2SO_4 , plates from H_2O , m. 189-90° to a red liquid, extinction 25-7°, α 1.525, γ 1.647; on slow crystn. there seps. together with the above form a monohydrate, needles with parallel extinction, α 1.583, γ 1.768+, 1.800-, seps. from alc. in the anhydrous form, has the same m. p. as the latter. **F** does not m. 300°, is readily decompd. by alkalis but is stable towards Na_2CO_3 , seps. in rectangular or hexagonal plates with sym. extinction, α 1.155+, γ 1.684; yield, 1.3-1.6 g. from 5 g. of the pseudo acid. *g*-Allylpseudoauric acid (3.5 g. from 5 g. uramil in 100 cc. of *N* KOH at 0° treated in the course of 1 hr. with 3 g. $\text{C}_6\text{H}_5\text{NCS}$), needles, turns pink 170°, m. 227-8° (decompn.), shows parallel extinction, α 1.591, γ 1.69; 3 g. with HCl

gives 2 g. 9-allyluric acid, does not m. 300°, seps. in plates with sym. extinction, α 1.75, γ 1.775, 1.80. Below are, resp., the habit, extinction and indexes (α and γ) for various compds. detd. during the course of this work: Urea, prisms, parallel, 1.4743, 1.6005; PhNHCONH_2 , plates, parallel, 1.602, 1.627; CO(NHPh)_2 , needles, parallel, 1.583, 1.74(?); NH(CONHPh)_2 , needles, parallel, 1.591, < 1.656 and > 1.649; allantoin, hexagonal plates, parallel, 1.579, 1.66—; uroxic acid, tetrahedrons, —, 1.5316, 1.6005; acid K uroxcinate, long needles, parallel, 1.4676, 1.629+; spiro-dihydantoin, hexagonal plates, 25–6°, 1.571—, 1.602; NH_4 chloroplatinate, thick hexagonal plates, isotropic, 1.8, —; methylammonium chloroplatinate, thin hexagonal plates, isotropic, 1.74, —. V. A third phenylbiuret. ELIZABETH S. GATEWOOD. *Ibid* 146–50.—Of the 2 known phenylbiurets, the one m. 165° is generally believed to be the unsym. compd. PhNHCONHCONH_2 (A), while to Weith's compd. (B), m. 190°, Schiff assigned the sym. structure PhN(CONH)_2 (C), chiefly because it gives the biuret reaction (C. A. 1, 1700). The newly discovered 3rd isomer (D) described in the preceding abstr. shows the biuret reaction, although not so strongly as B; it is apparently not an enol, $\text{PhNHC(OH):NHCONH}_2$, since it gives no color with FeCl_3 ; its formation from 9-phenyluric acid, in which the Ph group is on the N, seems to exclude such a structure as $\text{HN:C(OPh):NHCONH}_2$; ring formulas such as $\text{PhNHC(OH).NH.CO.NH}$ are improbable. Cer-

tain theoretical considerations (cf. preceding abstr.) made it seem desirable to assign to it the structure C. It was hoped to settle the question by synthesizing a true sym. biuret and $\text{PhN(CO}_2\text{Et)}_2$ was accordingly treated with NH_3 , but in H_2O there is no reaction while liquid or alc. NH_3 produce PhNHCO_2Et , and the question of the structures of B and D will have to be left open for the present. The most interesting property of D is that in even very dil. aq. soln. it can be transformed into A by NH_3 and a large no. of org. bases (NH_3Me , NHMe_3 , NH_2Et , NMe_2OH , PMe_2OH , SMe_2OH , IPh_2OH) but not by KOH , NaOH , Ba(OH)_2 or moist Ag_2O , although KOH effects the change incompletely if H_2O_2 is present; $\text{C}_6\text{H}_5\text{N}$ also does not bring about the reaction and PhCH_2NH_2 apparently reacts in some other way. PhNH_2 gives NH(CONHPh)_2 , obviously in consequence of a preliminary isomerization of the D into A. Against the possibility that D might be a "physical isomer" of A are the facts that A seems to be the more stable form, although it melts lower and is more sol., and that all the attempts to effect the reverse transformation (seeding of the satd. solns. or the melts and action of ultra-violet light upon the solids and their solns.) have hitherto failed. A, m. 165°, thin plates, α 1.572, γ 1.67, readily sol. in N alkali, difficultly in dil. HCl . B, m. 190°, short thick prisms, extinction 32–4°, α 1.532, γ 1.649+, is not isomerized by NH_3 . D, m. 196–8° (decompn.), long needles, extinction 32–3°, α 1.559, γ 1.73+, mol. wt. in freezing AcOH 146–58. The isomerizations were effected by adding a few drops of the base to a warm aq. suspension of the D, heating once to boiling and filtering. Warm dil. HCl does not change D. C. A. R.

Optical rotations of the sugars. I. The aldohexoses and aldopentoses. J. G. MALTY. *J. Chem. Soc.* 121, 2608–12 (1922).—The difference between the $(\alpha + \beta)/2$ values (the rotation due to the combined effects of the groups other than C atom 1, that concerned with the ketone formation) for epimeric aldopentoses and aldohexoses is const. and there is a similarity between pentoses and hexoses of similar configuration. In the case of mannose, idose and xylose, the value is 0 or negative, while in all the other cases it is positive. This gives a new method, dependent on the rotation, for classifying the sugars. If the rotations of the sugars in which the $(\alpha + \beta)/2$ value is positive are plotted, all the α , equil. and β values occur on the same vertical lines. Certain abnormal behaviors of the sugars are discussed in relation to their configurations. On equating the rotations and configurations given in the graph and solving in the manner applied to derivs. of the sugar acids, the mol. rotational value of each asym.

group is found; these are, for pentoses and hexoses: 5, —, —30°; 4, 60, 30; 3, 60, 60; 2, —60, —60; 1, ± 84, ± 84. Using these values it can be shown that allose and altrose should have the same rotations as mannose and glucose, resp. C. J. WEST

Mutarotation and pseudo-mutarotation of glucosamine and its derivatives. J. C. IRVINE AND J. C. EARL. *J. Chem. Soc.* 121, 2370-6(1922); cf. *C. A.* 7, 1490.—Tanret's "β-glucosamine-HCl" is shown to be a mixt. of 2 forms showing widely divergent sp. rotations. This mixt. can be fractionated by pptn. from C_6H_6 with EtOH or better by removing the α-form from aq. soln. by EtOH and then pptg. the β-form with Et_2O . The following initial values may be assigned the 2 forms: α, 100° → 72.5°; β, 25° → 72.6°. The behavior of the 2 forms on standing is illustrated by the following figures: After 3 min. of contact of solvent and solute: α, 97.9°, β, 32.60°; 14 min., 93.9°, 38.3°; 45 min., 84.7°, 51.1°; 20 hrs., 72.5°, 72.6°, const. This extensive upward mutarotation in the *d*-sense is an additional proof of the relation of glucosamine to glucose. The mol. rotation difference of the 2 forms is 16,160, which is of the order of that of glucose. The β-form reacts more readily with AcBr than the α-form. When triacetyl bromoglucosamine-HBr reacts with HOC_6H_4CHO , glucoside formation takes place only to a limited extent, the main reaction being condensation, forming *1-bromo-2-salicylidene-3,5,6-triacetylglucosamine*, brilliant yellow needles, m. 118°. That the Br is attached to a C atom and not as an additive mol. of HBr is seen from the behavior of the rotation in HO-contg. substances. The following initial and final observations were made: MeOH, 241.9°, 48.4°; EtOH, 197.7°, 51.1°; PrOH, 182.1°, 49.9°; iso-BuOH, 182.2°, 55.6°; AmOH, 169.5°, 54.5°; $PhCH_2OH$, 218.4°, 32.4°; $CH_3 : CHCH_2OH$ 192.8°, 75.6°; Me malate, 336.8°, 251.9°. On the other hand, in HO-free solvents the rotation was const.: HOC_6H_4CHO , 198.2° (The phenol OH of this compd. did not react with the solute as did the OH of all the other solvents used.); $CHCl_3$, 199.2°; AcMe, 195.2°; $AcOEt$, 177.7°. The general reactions involved in the pseudo-mutarotation were ascertained by examn. of the MeOH soln. After 6 days the chief constituent was found to be *2-salicylidene-3,5,6-triacetyl-1-methylglucosamine* (see next abstr.), while after several weeks the HBr formed in the reaction gave 1-methyl-3,5,6-triacetylglucosamine.

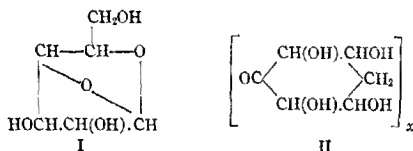
C. J. WEST

Salicylidene derivatives of *d*-glucosamine. J. C. IRVINE AND J. C. EARL. *J. Chem. Soc.* 121, 2376-81(1922); cf. preceding abstr.—When a glucosamine salt in H_2O is treated with alkali to liberate the free base and HOC_6H_4CHO added, the salicylidene deriv. generally seps. in the cryst. condition. The exception is methylglucosamine, which abnormal behavior may be explained by the cyclic formula previously suggested for this compd. *Salicylidene-glucosamine*, bright yellow needles, m. 183.5°, $[\alpha]_D$ in MeOH 11°. It is easily hydrolyzed by dil. acids. *2-Salicylidene-1-methylglucosamine*, bright yellow needles, m. 120°, $[\alpha]_D$ 2.2°; the yield is only 26%. The action of HNO_3 involves the removal of the $HOC_6H_4CH=$ group followed by the elimination of the NH_2 and MeO groups. *2-Salicylidene-3,5,6-triacetyl-1-methylglucosamine* was prepd. in 2 ways: the 1-Br deriv. in MeOH was treated with morphine or the triacetyl methyl deriv. was treated with HOC_6H_4CHO . The product forms pale yellow prismatic needles, m. 151-2°, $[\alpha]_D$ 75.7°. The 3 Ac groups were quant. removed by distn. with 15% H_2SO_4 . No $AcNH_2$ was formed after 4 hrs. treatment with EtOH- NH_3 . *2-Salicylidene-3,5,6-triacetyl-1-ethylglucosamine*, m. 131°, $[\alpha]_D$ 40.7°.

C. J. WEST

Cellulose chemistry. II: Action of dry hydrogen bromide on carbohydrates and polysaccharides. HAROLD HIBBERT AND H. S. HILL. *J. Am. Chem. Soc.* 45, 176-82 (1923); cf. *C. A.* 15, 1990.—As pointed out in the 1st paper the reactions of cellulose (A) are explained most satisfactorily on the assumption that it is a polymerized form of an anhydroglucose or cellulose "nucleus" (I). On the other hand, Cross and Bevan in the 1918 edition of their book (appendix, p. 334) still maintain that A is a ketonic

deriv. (II), chiefly on the basis of the work of Fenton and Gostling, who state that A and the ketoses give with dry HBr large amts. of ω -bromomethylfurfuraldehyde (B) and that the aldoses (glucose, etc.) yield only a trace of B. In view of the weighty theoretical considerations against C. and B.'s conception, the work of F. and G. was subjected to a careful, crit. reëxamn. and results differing in most cases appreciably from theirs were obtained. Below are given the yields (in g. per 10 g. carbohydrate) of crude B crystals obtained by H. and H. and by F. and G., resp., from various substances: A (surgical cotton) 5.6, 3.3; A (viscose) 5.5, —; cellobiose 2.7, —; α -Me glucoside (m. 156°) 1.5, —; cane sugar 3.5, 0.85; glucose 1.2, 0.3 (sirup); lactose 0.7 (crystals and sirup), 0.3 (sirup); galactose 0.3 (crystals and sirup), 0.3 (sirup). These results show that F. and G.'s reaction is of no value as a criterion for the presence of ketose and the absence of aldose derivs. If Hübner's view of the structure of A is correct, it would seem that the high yield of B from A and the low yield (none, according to F. and G.) from glucose is probably to be associated with the fact that in A there is no free, reactive aldehyde group capable of interfering with the reaction. This is confirmed by the relative yields (56, 27 and 12%) from A, cellobiose and glucose, resp., which have 0, 0.5 and 1 aldehyde group, resp., for each glucose unit. Further confirmation is afforded by the somewhat higher yield from α -Me glucoside as compared with glucose. The formation of B is also apparently inversely proportional to the ease of hydrolysis of the carbohydrate, but various factors other than hydrolysis play an important role, as indicated by the remarkable difference in the yields from the stereoisomeric cellobiose and lactose. The yields given above are the wts. of the residues obtained by complete evapn. of the neutralized CHCl_3 soln.; if allowed to stand for a day or two they change completely to a black rubbery mass. Probably much of the impurity in the crude residues consists of decompn. products of B and therefore the wts. of the residues probably represent fairly accurately the actual amts. of B originally present. When pure, B is stable for quite a long time. Attempts to increase the yields of B by varying the time of heating or the concn. of the CHCl_3 soln. of the HBr, by using different solvents (Et_2O , Pr_2O , Bu_2O , in which HBr is more sol. than in CHCl_3), or moist CHCl_3 and by employing catalysts (FeCl_3 , I, CaCl_2 , ZnCl_2 , $(\text{CO}_2\text{H})_2$, moisture) failed. ZnCl_2 appears to inhibit completely the action on A.



C. A. R.

Friedel-Crafts reaction. HEINRICH WIELAND AND LUDWIG BETTAG. *Ber.* 55B, 2246-55 (1922).—W. and B. feel that the present work affords definite proof of the correctness of the assumption of Darzens (C. A. 4, 2093) that the principle of the primary addn. of alkyl or acyl chlorides to olefin double bonds, in the presence of AlCl_3 , followed by elimination of HCl, holds for the aromatic series also. Cyclohexene (A) and $\text{Me}_2\text{C}=\text{CHMe}$ (B) yield with AcCl and BzCl satd. β -chloroketones, which are freed with KMnO_4 from the unsatd. ketones formed simultaneously and purified through their semicarbazones; treated under the conditions necessary for the Friedel-Crafts synthesis, i. e., allowed to react at a slowly rising temp. with AlCl_3 in CS_2 , these chloroketones lose HCl and yield the normal end products of the reaction, viz., the unsatd. ketones. The difference between olefins and C_6H_6 derivs. in this reaction is only one of degree; the much more reactive aliphatic double bond permits of the formation of the primary addn.

product under conditions under which it is to some extent stable, while in the aromatic series the much more sluggish double bond allows of the addn. only under conditions which at the same time favor the elimination of HCl. The catalytic action of the AlCl_3 is believed to be due to its formation with the acyl chloride of a complex

R
|
(AlCl_3)...($\text{C} : \text{O}$).Cl or (AlCl_3)...CO.R

which results in a loosening of the union between the Cl and the C and thus enables both addenda to add; the ease with which the primary satd. product decomp. is also probably due to the tendency of the AlCl_3 to form complexes. Attempts to obtain as clear a picture of the course of the reaction in the hydrocarbon synthesis by the F.-C. method were not so successful; the alkyl halides react so slowly that the polymerizing action of AlCl_3 on olefins, which leads to resinous products, becomes the chief reaction, and, moreover, the newly formed alkyl halide disturbs the original reaction in that it, too, strives to combine with the olefin.

2-Chlorocyclohexyl methyl ketone, light yellow oil of faintly irritating, PhCOME-like odor, b_1 60–3° (slight decompn.), turns yellow-brown in a few days, is prepd. by treating 20 g. A in 75 g. dry CS_2 (purified by shaking with Hg, then with cold satd. HgCl_2 and finally with cold satd. KMnO_4) at –18° in the course of 2 hrs. with 35 g. AlCl_3 , cautiously decompg. with ice, extg. with Et_2O , shaking with NaHCO_3 , drying with Na_2SO_4 and fractionating; the fraction b_1 65–78° (15.8 g. with 13.98% Cl) is oxidized in 150 cc. cold Me_2CO with powdered KMnO_4 , filtered, decolorized with SO_2 , extd. with Et_2O and shaken with NaHCO_3 , giving on evapn. 6.45 g. crude product (21.01% Cl); semicarbazone (2.21 g. from 2.65 g. of the ketone), leaflets from 1 : 1 MeOH-EtOH + boiling H_2O to incipient turbidity, m. 163° (decompn.); 2.1 g. gently warmed with 30 g. of 2 N H_2SO_4 gives 1.4 g. of the pure ketone; 10.25 g. of the ketone in 25 g. CS_2 in a freezing mixt. treated with 0.5 g. AlCl_3 , slowly allowed to rise to room temp. and heated until the evolution of HCl slackens, the process being repeated with further addn. of 2.5 and 3.0 g. AlCl_3 until, after 10 hrs., no HCl is evolved on the H_2O bath, gives 7 g. of a dark yellow liquid, b_1 74–92°, consisting chiefly of tetrahydroacetophenone. *2-Chlorocyclohexyl phenyl ketone*, obtained in 13% yield from A and BzCl , thick, light yellow oil of faint pleasant odor, b_1 120–2° (slight decompn.); treated with AlCl_3 as described above for the Me compd., 10 g. evolves only 45.14% of the calcd. amt. of HCl and treatment of the product, after decompn. with ice, with Et_2O leaves undissolved considerable amts. of a red amorphous substance (doubtless polymerization products); fractionation of the Et_2O ext. gives 6 g. of a thick light yellow oil, b_1 126–30°, still contg. much Cl (12.58–13.37%) and yielding only a minimal amt. of tetrahydrobenzophenone semicarbazone, faintly yellowish prisms from alc., m. 213° (decompn.); this is also obtained in only 0.8% yield directly from A and BzCl by the F.-C. method without isolating the intermediate product. *Chloro-sec-isoomyl methyl ketone* (3.65 g. from 10 g. B and 14 g. AcCl), light yellow liquid of camphor-like, somewhat irritating odor, begins to darken and lose HCl within a few hrs., 5% decomp. in 34 hrs.

C. A. R.

Formation and properties of dithioketones ($\text{R}_2\text{C}:\text{S}:\text{S}$) and dithio-ethers ($\text{R}_2\text{S}:\text{S}$).

- III. K. G. NAIK AND M. D. AVASARE. *J. Chem. Soc.* 121, 2592–5 (1922); cf. C. A. 15, 2072, 3621.—This work was undertaken to test the hypothesis that interaction of S_2Cl_2 and a compd. contg. the $\text{CH}_2=\text{}$ radical depends upon the nature of the groups attached to the 2 remaining valences of the C atom. *Dithioacetacetamidide*, by heating $\text{AcCH}_2\text{CONHPh}$ with S_2Cl_2 in C_6H_6 , m. 125° (decompn.). *Dinitro derivative*, brown powder, decomp. 167°. *Acetoacet-p-toluidide*, m. 95°. *Dithio derivative*, m. 140° (decompn.). *Dinitro derivative*, yellow powder, decomp. 170°. *Acetoacet-o-toluidide*, m. 107°. *Dithio derivative*, decomp. 167°. The reactivity increased in the order of the compds. described, which is in accordance with the theory. C. J. WEST

Preparation of aryl isothiocyanates. F. B. DAINS, R. Q. BREWSTER AND C. P. OLANDER. *Univ. Kansas Sci. Bull.* 13, 1-14 (1922).—Aromatic mustard oils (A) have been prepd. by synthesizing disubstituted thioureas (B) from amines, followed by splitting into A and the amine, but the yields are low (*Ber.* 15, 986 (1882)). Ac_2O or AcCl interacts with B and then the Ac deriv. readily breaks up into A and an arylacetyl chloride (*J. Chem. Soc.* 59, 400 (1891)); *J. Am. Chem. Soc.* 22, 188 (1900)), but by this method only 0.5 of the original amine can be converted into A. A second general method depends on the intermediate formation of salts of substituted dithiocarbamic acid, RNHCSSMe (cf. Anschütz, *C. A.* 4, 1476, 2120). In the aromatic series, compds. as $\text{RNHCSSNH}_2\text{R}$ cannot usually be isolated, losing H_2S and yielding compds. as RNHCSSNHR . Yet arylamines with CS_2 and NH_3 give quant. the NH_4 salts, RNHCSSNH_4 , which should yield A provided NH_4SH could be removed readily. In this matter, Andreacchi (*Ber.* 36, 3520 (1903)) showed that NH_4 dithiocarbamates with ClCO_2Et gave A but that the compds. produced contained oxygen ureas as impurities; and furthermore the reagent is expensive. Losanitsch (*Ber.* 24, 3021 (1891)) prepd. from PhNHCSSNH_4 (C) in H_2O six metallic salts. He indicated that PhNCS (D) may be quant. prepd. by distg. C with CuSO_4 and steam. Heller and Bauer (*J. prakt. Chem.* [2] 65, 365 (1902)) prepd. A, using PbCO_3 and NH_4 aryl dithiocarbamates. D. et al. show that the L. method is generally applicable for the prepn. of A. Using a modified H. and B. method (*loc. cit.*), to 54 g. CS_2 and 28% NH_4OH (80 g.) in an iced beaker, 54 g. PhNH_2 were added during 15 min. with const. stirring. C sepd., and after standing 1 hr. in ice was filtered, washed with alc. and dried on a porous plate. On standing, H_2S , NH_3 , CS_2 , PhNH_2 and thiocarbamide (E) were formed, the decompn. being hastened when the salt was boiled with H_2O . $\text{C} = \text{PhNH}_2 + \text{CS}_2 + \text{NH}_3$ and $\text{C} = \text{D} + \text{H}_2\text{S} + \text{NH}_3$. In the case of the NH_4 salts of *p*-chloro- and *p*-bromophenyl dithiocarbamates, where the amines and the A are less volatile, 55-60% yields of the substituted E were obtained. With HCl the equation is: $\text{C} + 2\text{HCl} = \text{PhNH}_2\text{HCl} + \text{CS}_2 + \text{NH}_4\text{Cl}$ (quant.). To produce A from RNHCSSNH_4 a salt must be used which will give a stable sulfide and an NH_4 salt. FeSO_4 , ZnSO_4 , CuSO_4 and $\text{Pb(NO}_3)_2$ with C gave after standing and distn. with steam a 3 cc., 23%, 71.7% and a 77.2% yields, resp., of D. Directions for the prepn. of D in the lab. are given. CS_2 (54 g.) and 80 g. concd. NH_4OH in a beaker surrounded by ice are stirred by a turbine. PhNH_2 (56 g.) is dropped from a separatory funnel during 20 min. C then seps. and the mixt. is stirred 30 min. after the PhNH_2 is added, and then allowed to stand 30 min. without stirring. Dissolve the C in 80 cc. H_2O , add with stirring 200 g. $\text{Pb(NO}_3)_2$ in 400 cc. H_2O and steam distil from a 5-l. flask. Put dil. H_2SO_4 in the receiver to combine with NH_3 and PhNH_2 , —to prevent formation of $(\text{PhNH})_2\text{CS}$. Directions are also given for large-scale production. PhNHCSSNa in H_2O was treated with $\text{Pb(NO}_3)_2$ but only a 30.2% yield of D was obtained. The Ba salt and ZnCl_2 gave a 37.4% yield, and in the case of the Ca salt very little D was formed, the main product being E. The method was used for the prepn. of the following isothiocyanates: *o*- (73.27% yield), *m*-, *p*-tolyl, 1,3,4-xylyl, *m*. 31°, pseudocumyl, α - and β -naphthyl, *o*- and *p*-anisyl and *p*-phenetidyl. *m*- and *p*-Bromophenyl, *p*-chlorophenyl, and *p*-iodophenyl derivatives were also formed. All efforts to prep. *p*- $\text{O}_2\text{NC}_6\text{H}_4\text{NHCSSNH}_4$ failed, the *p*- $\text{O}_2\text{NC}_6\text{H}_4\text{NH}_2$ was recovered unchanged. The success of the method is dependent on the completeness of the formation of RNHCSSNH_4 , on the ease and completeness of sepn. from the sulfide ppt. and on the avoidance of side reactions. The cause of the failure with β - $\text{C}_6\text{H}_4\text{NH}_2$ must be investigated.

H. E. WILLIAMS

Isothiourea ethers. F. B. DAINS AND W. C. THOMPSON. *Univ. Kansas Sci. Bull.* 13, 118-20 (1922).—Substituted thioureas add alkyl halides directly (*Ber.* 14, 1490 (1881); 15, 1314 (1882); 21, 962, 1857 (1888)): $\text{RNHCSSNHR} + \text{R}'\text{X} = \text{RNHC}$

(SR')NR.HX, and from these salts the free thiourea ethers can be prepd. by the action of alkalis. The synthesis of the Pr and Bu ethers of certain thioureas is reported. When 15 g. thiocarbanilide, and 10 g. PrI were heated 1 hr. on the steam bath, the light brown viscous liquid which sepd. solidified on cooling and when crystd. from alc. γ -propyl- α,β -diphenylthiourea hydroiodide was obtained, colorless crystals, m. 103°, slightly sol. in Et₂O, cold H₂O and cold alc., but readily sol. in hot H₂O, alc. and Me₂CO. When treated with aq. NaOH, the free base was formed, insol. in H₂O, needles from alc. m. 61.5°. When BuI and (PhNH)₂CS were heated on the steam bath for 1 hr. the salt which solidified on cooling could not be purified by crystn. It was ground up, washed with Et₂O in which it was entirely insol. This was γ -butyl- α,β -diphenylthiourea hydroiodide m. 122°, and with Na₂CO₃ the free base was formed, heavy colorless oil, readily sol. in the ordinary org. solvents. PrI and (*p*-PhCH₂NH)₂CS gave γ -propyl- α,β -di-*p*-tolyl thiourea hydroiodide m. 165°, purified by washing with cold alc. The free base was pptd. by the addn. of alkali, fine, white needles from alc., m. 99°. The corresponding butyl derivative of the salt m. 145° and the free base is a thick, colorless liquid insol. in H₂O but sol. in org. solvents. Di-*m*-xylylthiourea and PrI reacted easily on warming and the product was the free base (not the salt), γ -propyl- α,β -di-*z*,*z*-dimethylphenylthiourea, purified from alc. m. 113.5°. The unsym. nature of the mol. did not prevent addn. of the alkyl iodide, for MeI and PhNHCSNHCH₂Br (B) when heated gave γ -methyl- α -*p*-bromophenyl- β -phenylthiourea hydroiodide, m. 152°, and in alc. the salt when treated with Na₂CO₃ gave the free base white needles m. 79°. When B and PrI were mixed γ -propyl- α -*p*-bromophenyl- β -phenylthiourea hydroiodide was formed as a heavy red oil. The free base from alc. m. 84°. B with BuI gave γ -butyl- α -*p*-bromophenyl- β -phenylthiourea hydroiodide thick non-crystallizable oil, from which with alkalis the free base, viscid oil, sol. in alc. and Et₂O, was obtained. When PhNHCSNH₂ and BuI were warmed on the bath a gummy mass resulted which was dissolved in hot alc. and neutralized with Na₂CO₃. On diln. with H₂O a heavy oil, γ -butylmonophenylthiourea sepd.

H. E. WILLIAMS

Addition reactions of phosphorus halides. VI. The 1,2- and 1,4-addition of diphenylchlorophosphine. J. B. CONANT, J. B. S. BRAVERMAN AND R. E. HUSSEY. *J. Am. Chem. Soc.* 45, 165-71 (1923); cf. *C. A.* 17, 273.—Ph₂PCl reacts like PCl₃ or PhPCl₂ with BzH or PhCH : CHCOPh (A), in the presence of AcOH or Ac₂O, giving AcCl and the phosphine oxide, PhCH(OH)POPh₂ (B) or PhCH(POPh₂)CH₂COPh (C). That it adds in the 1,4-position to a typical α,β -unsatd. ketone (A) was shown by carrying out the reaction in Ac₂O free from AcOH; the intermediate product (D) was not isolated in cryst. form but its reactions are best represented by the structure $O(PPh_2)_2O.CPh : CH.CHPh)_2$; with H₂O it gives C; in CHCl₃ or Ac₂O it combines with

2 equivs. of Br without evolution of HBr; the resulting dihydromide was not obtained cryst. but with H₂O gave a mixt. of 2 stereoisomeric mono-Br oxides, PhCH(POPh₂)CHBrCOPh (E). Since PCl₃, PhPCl₂ and Ph₂PCl all react alike, combination with C : O compds. (under suitable conditions) may be considered a general reaction of the halides of tervalent P. Of the 2 forms of E (and of the corresponding dihydromides of the *p*-ClC₆H₄COCH : CHPh series) the high-melting form with alc. NaOH at room temp. gives an unsatd. oxide, PhC(POPh₂) : CHCOPh (F), which is reduced to C by Zn and AcOH, while the low-melting forms are reduced to C by alc. NaOH; both reactions are almost quant. With KOAc in boiling alc., on the other hand, the high-melting form of E is quant. reduced to C and the low-melting form partially converted into F. The fact that both forms can yield either C or F, depending on the reagent employed, indicates that they are stereoisomers. α -Hydroxybenzylidiphenylphosphine oxide (B), from 5 g. BzH in 3 g. AcOH allowed to stand 30 min. with 10.4 g. Ph₂PCl, crystals from PhMe, m. 230°, stable towards mild oxidizing agents but gives some BzH with

CrO_3 in warm H_2SO_4 . α -Phenyl- β -benzoylthiophenylphosphine oxide (C) (7.6 g. from 5 g. A in 1.5 g. in AcOH and 5.3 g. Ph_2PCl), cryst. powder from alc., m. 227° . β -*p*-Chlorobenzoyl analog (G) (3.8 g. from 2.4 g. $\text{ClC}_6\text{H}_4\text{COCH} : \text{CHPh}$), m. $225-6^\circ$. α -Phenyl- β -bromo- β -benzoylthiophenylphosphine oxides (E): High-melting form (also obtained in good yield from C and Br refluxed 30 min. in CHCl_3), m. 187° ; low-melting isomer, obtained in 1.6 g. yield, together with 1.2 g. C and 0.7 g. of the high-melting bromide, from 5.3 g. Ph_2PCl and 5 g. A (dried over P_2O_5) allowed to stand 1 hr. with 1.25 g. Ac_2O , treated with Br in Ac_2O , poured into H_2O after 10 min. and allowed to stand overnight, m. 158° , is more sol. in alc. than its isomer and can be sepd. from it by repeated crystn. β -*p*-Chlorobenzoyl analogs: High-melting form, obtained in 1.2 g. yield, together with 3.9 g. of its isomer, from the addn. product of 3.2 g. $\text{ClC}_6\text{H}_4\text{COCH} : \text{CHPh}$ and Ph_2PCl brominated in Ac_2O and then treated with H_2O , m. 196° ; low-melting isomer, also obtained from G boiled 3 hrs. with Br in CHCl_3 , m. 187° . α -Phenyl- β -benzoylvinylthiophenylphosphine oxide (2 g. from 3 g. of the E m. 187° in alc. allowed to stand 1 hr. with concd. aq. NaOH , poured into H_2O , acidified and allowed to stand overnight), pale yellow crystals, m. 143° , reduces KMnO_4 in Me_2CO but does not combine with Br or HBr in AcOH , combines with dry O_2 in CHCl_3 . β -*p*-Chlorobenzoyl analog, yellow needles, m. 151° , obtained almost quant. from the high-melting bromide with alc. NaOH and in 78% yield from the low-melting isomer boiled in alc. 3 hrs. with KOAc .

C. A. R.

Aromatic sulfonyl chlorides. JESSIE STEWART. *J. Chem. Soc.* 121, 2555-61 (1922).—Since the use of PCl_5 is somewhat troublesome when applied to large quantities and SOCl_2 is not always applicable, the possibility of using ClSO_2H , suggested by the literature, was tried. In the majority of the cases studied the results have been entirely satisfactory. 2,5-Dichlorobenzenesulfonyl chloride was obtained in 85% yield from p - $\text{C}_6\text{H}_4\text{Cl}_2$ and SO_2HCl at 150° for 1 hr.; needles, m. 39° . Reduced with Zn dust in a mixt. of AcOH-HCl and treated with FeCl_3 , it gave 2,5,2',5'-tetrachlorodiphenyl disulfide, needles, m. $81-2^\circ$. Acetanilide-*p*-sulfonyl chloride, by heating a soln. of PhNHAc in 5 mols. SO_2HCl at 60° for 2 hrs., needles, m. 149° . 3-Chlorosulfonyl-*p*-tolyl methyl ether, prepd. from p - $\text{MeOC}_6\text{H}_4\text{Me}$ and SO_2HCl , or from the 3- SO_3H deriv., needles, m. 84° . The amide m. 193° . 4,4'-Dimethoxydi-*m*-tolyl disulfide, pale yellow prisms, m. 67° . 5-Chlorosulfonylsalicylic acid, prisms, m. $169-71^\circ$. Contact with H_2O must be avoided as much as possible in order to obtain a good yield (60%). 5-Sulfinosalicylic acid, best prepd. by reduction with aq. Na_2SO_3 , needles, m. 159° . 5,5'-Dithiosalicylic acid, pale yellow powder, m. 236° . 5-Thiolsalicylic acid, by reduction of the disulfide with glucose or hydrolysis with 8 mols. N NaOH , pale yellow microneedles, m. $150-2^\circ$. 5-Methylthiolsalicylic acid, pale buff powder, m. 126° . 4-Chlorosulfonylcinnamic acid, needles, m. 226° . The constitution was established by conversion into the amide, m. $250-80^\circ$ (Palmer, *Am. Chem. J.* 4, 163). Chlorosulfonylphenylacetic acid, prisms, m. 136° . The max. yield is about 35%. Amide, shining plates, m. 176° .

C. J. WEST

Labile nature of the halogen atom in organic compounds. VI. The action of titanous chloride and of ammonia on representative halogen compounds. I. A. BLACK, E. L. HIRST AND A. K. MACBETH. *J. Chem. Soc.* 121, 2527-33 (1922); cf. C. A. 17, 91.—The earlier work has been extended to det. if the halogen atoms in the compds. studied are susceptible to reduction by titanous salts and if the oxidizing power of these substances is sufficient to liberate N from NH_3 . The *N*-halides are found to be readily reduced by solns. of TiCl_3 . $\text{PhS(O}_2\text{K)} : \text{NCl}$, PhNHCl , AcNHBr , 2,4- $\text{Me}_2\text{C}_6\text{H}_3(\text{NO}_2)_2\text{S(O}_2\text{K)} : \text{NCl}$ and $\text{CHBr}(\text{CONH}_2)_2$ required 2 atoms of H for the reduction of a gram-mol. Compds. of the type RSO_2NX_2 required 4 atoms, as did $\text{CBr}(\text{CONH}_2)_2$; $\text{CHNO}_2(\text{CO}_2\text{Et})_2$ required 6 atoms and $\text{BrC(NO}_2)(\text{CO}_2\text{Et})_2$ required 8 atoms. CH_2Br -

NO_2 is not reduced by TiCl_3 or N_2H_4 , while $\text{CHBr}(\text{CO}_2\text{Et})_2$ is only partially reduced after prolonged treatment. It is found that NH_3 is readily oxidized by many *N*-halides, probably quant. The results are slightly low and the method cannot be recommended. Succinchloro- and -bromoimides react vigorously. There was no action with the bromomalonic esters or amides, the halogen derivs. of diketones or compds. of the type of chloramine-T. VII. Absorption spectra of the halogen derivatives of some cyclic compounds and their bearing on the question of an oxygen-halogen linking. HUGH GRAHAM AND A. K. MACBETH. *Ibid* 2601-8; cf. *C. A.* 16, 2848.—The earlier observations have been extended to other types of compds. contg. reactive halogen atoms, and the results obtained furnish further support for the view that an *o*-halogen linking does not occur in the reactive substances. The absorption spectra of the Cl_2 and Br_2 as well as the CIBr deriv. of 1,1-dimethylcyclohexane-3,5-dione differ entirely from those of the parent substance, the monohalogen derivs. and the Na salts. The absorption curves of cyclohexanespirocyclohexane compds. are practically identical with the graphs of the corresponding 1,1-dimethylcyclohexane deriv. The absorption spectra of some *N*-haloids and the corresponding parent compds. are shown; the halogen derivs. show absorption of much the same type as that of the compds. from which they are derived, an increase in general absorption being noted in all cases examd. The introduction of the halogen atom into these substances appears to produce no radical change in the constitution of the compds. and therefore the reactivity is not to be explained on such grounds.

C. J. WEST

Attempts to prepare red sulfide dyes. II. Mercaptan derivatives of azo dyes. E. R. WATSON AND SIKHIBHUSHAN DUTT. *J. Chem. Soc.* 121, 2414-9(1922); cf. *C. A.* 16, 4212. —*m*-Hydroxyphenyl mercaptan (A), prepd. by heating the xanthate (from $m\text{-HOC}_6\text{H}_4\text{N}_2\text{X}$ and KSCSOEt at 70°) with Zn and HCl, pptg. as the Pb salt and decomg. with H_2S , yellow oil. FeCl_3 in excess gave *di-m*-hydroxyphenyl disulfide, hexagonal plates, m. $85-90^\circ$. A, coupled with $(\text{C}_6\text{H}_4\text{N}_2\text{X})_2$, gave diphenyl-4,4'-bisazo-hydroxy-2-phenyl mercaptan, sol. in Na_2S and dyes cotton red which is oxidized to brownish yellow in the air. The color is not as fast to alkalis as that of ordinary yellow sulfide dyes. 1-Hydroxy-5-naphthyl mercaptan, softens 105° , m. 115° . FeCl_3 gives 1,1'-dihydroxy-5,5'-dinaphthyl disulfide, m. $190-200^\circ$. Diphenylbisazo-1-hydroxy-5-naphthyl mercaptan, only slightly sol. in Na_2S and does not dye cotton well from a Na_2S bath. 2-Hydroxy-7-naphthyl mercaptan, m. $60-70^\circ$. Diphenylbisazo-2-hydroxy-7-naphthyl mercaptan, almost insol. in Na_2S . The corresponding xanthate, $[\text{C}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4(\text{OH})\text{SCSOEt}]_2$, purple, is sol. in Na_2S and dyes dull maroon shades on cotton but the affinity for cotton is not great. 3-Nitro-4-ithiolbenzenesazo-4-hydroxy-2-phenyl mercaptan, $\text{O}_2\text{NC}_6\text{H}_3(\text{SH})\text{N}_2\text{C}_6\text{H}_4(\text{OH})\text{SH}$, from $\text{O}_2\text{NC}_6\text{H}_4(\text{SH})\text{N}_2\text{X}$ and A, dyes fairly good brown shades on cotton. Benzenesazothioresorcinol, dyes cotton yellowish brown. Thio-benzidine, by heating $(\text{C}_6\text{H}_4\text{NH}_2)_2$ with S at $180-200^\circ$ for 12 hrs., yellow, m. $265-70^\circ$ (decompn.). Diazotized and coupled with Schäffer's salt, it gave disulfidodiphenyl-bisazo- α -naphthol-2-sulfonic acid, $\text{C}_{20}\text{H}_{16}\text{O}_4\text{N}_4\text{S}_2$, crimson, dyes cotton directly and also from a sulfide bath. While faster than most direct cotton dyes the colors are not as good as ordinary sulfide dyes. Di- α -naphthol trisulfide, $(\text{C}_{10}\text{H}_7\text{OH})_3\text{S}_3$, formed by dissolving 4 atoms S in a soln. of 1 mol. $\text{C}_{10}\text{H}_7\text{OH}$ in aq. NaOH, couples with $(\text{C}_6\text{H}_4\text{N}_2\text{X})_2$, giving a dye sol. in NaOH and Na_2S , which dyes cotton only in light clay-colored shades from a sulfide bath.

C. J. WEST

Derivatives of diphenylthiolbenzene. SAMUEL SMILES AND HUGH GRAHAM. *J. Chem. Soc.* 121, 2506-10(1922).—A comparison is made of the behavior of *o*-dithiobenzoic acid with other typical aromatic disulfides. *m*-Dithiobenzoic acid, condensed with C_6H_6 by means of concd. H_2SO_4 , gave benzenedi-*m*-thiobenzoic acid, $\text{C}_6\text{H}_4\text{-(SC}_6\text{H}_4\text{CO}_2\text{H)}_2$, micropowder, m. $302-3^\circ$, best purified through the sodium salt, broad

prisms with H_2O of crystn. *Naphthalenedi-m-thiobenzoic acid*, small yellow needles, m. $256-8^\circ$ (decompn.). *Benzenedi-p-thiodimethylaniline*, broad needles, m. $171-2^\circ$. *p-Xylenedi-p-thiodimethylaniline*, needles, m. $232-3^\circ$. The soln. in AcOH rapidly assumes a violet color, owing to oxidation. *p*-Thiodimethylaniline may be recovered unchanged after its soln. in H_2SO_4 has been kept at 20° but reaction begins at once when the hydrocarbon is added. These products are not attacked by reducing agents.

C. J. WEST

The mobility of symmetrical triad systems. I. The conditions relating to systems terminated by phenyl groups. C. K. INGOLD AND H. A. PIGGOTT. *J. Chem. Soc.* 121, 2381-9(1922).—A comparative study is made of the mobility of sym. tautomeric systems of the general formula $(H)XY : X$. The proof of the mobility of the N -systems present in $NHPhN : NPh$ and in $NHPhCH : NPh$ rests on the proof that only a single substitution product exists where 2 might be expected, and that this individual, on fission at the double bond, gives 4 products. These tests failed when applied to compds. of the type $CH_2PhN : CHPh$. From the close relationship of $CH_2PhCH : CHPh$ to glutaric acid, it was expected that it would behave in the same way, but it was found that the 2Ph groups are not equiv. It is seen that the activating condition (in a potentially tautomeric system) is dependent primarily upon the α -atom of the system and is associated with the easy detachment of H from this position and that this condition is one of the well recognized group of related characteristics generally supposed to be associated with negative elec. polarity. *Benzylidene-p-nitrobenzylamine*, dense prisms, m. 71° ; *m*-derivative, short, dense prisms, m. 42° ; *p*-nitrobenzylidene-*m*-nitrobenzylamine, needles, m. 115° . *p*-Nitrobenzylidenebenzylamine, laminas, m. 56° . *m*-Derivative, long, thin laminas, m. 62° . *m*-Nitrobenzylidene-*p*-nitrobenzylamine, needles, m. 115° . These are stable towards alkali and H_2O but are hydrolyzed into their components by mineral acids. The condensation of $PhCH_2CH_2CO_2Na$ and *p*-MeOC $_6$ H $_4$ CHO by heating with Ac_2O for 9 hrs. at 150° gave α -phenyl- γ -*p*-methoxyphenyl- Δ^2 -propene, b $_p$ 227° (dibromide, stout prisms terminated by pyramide, m. 115°), and *p*-methoxy- α -benzylcinnamic acid, sepd. from the cinnamic acid by its insol. in Na_2CO_3 , flattened needles, m. 170° . It instantly decolorizes cold $KMnO_4$, giving $PhCH_2OH$, $BzOH$ and *p*-MeOC $_6$ H $_4$ CO $_2$ H. *Anilide*, long, silky needles, m. 159° . γ -Phenyl- α -*p*-methoxyphenyl- Δ^2 -propene, b $_p$ 220° ; dibromide, prisms, m. 76° . *o*-*p*-Methoxybenzylcinnamic acid, glistening needles, m. 165° . Cold alk. $KMnO_4$ gives *p*-MeOC $_6$ H $_4$ CH $_2$ CO $_2$ H, *p*-MeOC $_6$ H $_4$ CO $_2$ H and $BzOH$. *Anilide*, short, thick prisms or needles, m. $140-1^\circ$.

C. J. WEST

Solubility and volatility of the nitrobenzaldehydes. N. V. SIDGWICK AND W. M. DASH. *J. Chem. Soc.* 121, 2586-92(1922).—Because the NO_2 and CHO groups are often found in the most markedly abnormal C_6H_5 derivs., the $O_2NC_6H_4CHO$ have been examd., in which the 2 groups occur together. The soly. was measured in sealed bulbs or at lower temps. in a Beckmann app. The temp. of the triple point in presence of H_2O was detd. in a series of sep. expts. and the compn. obtained by extrapolation. The complete soly. curves were realized in H_2O for the *m*- and *p*- compds., with critical soln. temps. of 212° and 216° , but the *o*-curve could not be taken above 160° , as decompn. then set in. Results are given for H_2O and C_6H_6 . The volatility in steam (wt. % in distillate) was found to be: *o*, 1.89; *m*, 1.27; *p*, 0.85. The nominal heats of soln. in C_6H_6 were calcd. from the soly. curve by means of the usual formula and the results plotted. The influence of position on the phys. properties of the $O_2NC_6H_4CHO$ is not large. To be abnormal, the isomers must contain a group making them sensitive and another group which can act on this sensitiveness.

C. J. WEST

Chlorination of benzoyl chloride. I. EDW. HOPE AND GEO. C. RILEY. *J. Chem. Soc.* 121, 2510-27(1922).—The following b. ps. at reduced pressures were detd. on pure

materials: BzCl: 9 mm., 71°; 10.5, 75°; 13, 79°; 15.5, 82.5°; 19.5, 87°; 25, 92.5°; 28, 94.5°; 35.5, 100.5°; *o*-ClC₆H₄COCl: 11 mm., 101.5°; 12, 103.5°; 12.75, 105°; 14.5, 108°; 19.75, 114.5°; 26.5, 122°. *m*-ClC₆H₄COCl: 10 mm., 94.5°; 12.5, 99.5°; 15, 103.5°; 19, 109.5°; 21, 112°; 26, 117.5°. *p*-ClC₆H₄COCl: 10.5 mm., 97.5°; 11.5, 99°; 15, 104.5°; 18.5, 109°; 27.5, 119°. The action of Cl upon BzCl in the absence of a carrier appeared to give a hexachloride. In the presence of anhydrous FeCl₃ at 35°, however, the Cl was much more rapidly absorbed (106 g. in 5.75 hrs.), the main product of the reaction being *m*-ClC₆H₄COCl. The reaction product was fractionally distd. *in vacuo* and the fractions were hydrolyzed to the corresponding acids. The estimation of the proportions in which the different acids were present in the mixt. after hydrolysis was carried out by means of a series of solidification-point detns., details of which are given. The result of the fractionation and analysis indicated that 13.5% BzCl was recovered unchanged and that 76% mono-Cl and 5% di-Cl compds. were formed. Of the mono-Cl compds. 83.5% was *m*-, 14.5% *o*- and 2% *p*-ClC₆H₄COCl. 2,5-Cl₂C₆H₃CO₂H was isolated in the pure condition. In the lab. prepn. of *m*-ClC₆H₄COCl, comparatively pure material is found in the fraction b₁₂ 99°. For the greatest yield of the *m*-acid, the whole fraction b₁₂ 96-118° is hydrolyzed, the acid converted into the Ba salt and fractionally crystd. from H₂O. A more rapid method is to collect the fraction b₁₂ 97-102°, hydrolyze, and cryst. from 30% AcOH, then from C₆H₆.

C. J. WEST

Triazo group. XXII. Cinnamic acid chlorohydrin and its conversion into α -triazio- β -phenylpropionic acid. M. O. FORSTER AND WM. B. SAVILLE. *J. Chem. Soc.* 121, 2595-601 (1922); cf. *C. A.* 7, 329.—This work is a part of the synthesis of picrorocellin (*C. A.* 16, 2517). In repeating the work of Read and Andrews (*C. A.* 16, 419) on the action of Cl on PhCH:CHCO₂H, no dichloride and very little chlorostyrene were found, a 73% of the chlorohydrin being obtained and a neutral by-product, *chlorostyrene chlorohydrin*, PhCH(OH)CHCl₂, massive transparent rhomboidal prisms, m. 56°, being found in small amts. Protection from sunlight merely retarded the reaction without altering its character or yield of the products, while in a dull red light the reaction proceeded very slowly. A modification of the method of Erlenmeyer and Lipp (*Ann.* 219, 185), using NaOCl, in which larger quantities may be used, gave a 72% yield; the by-product was chlorostyrene. The true m. ps. of the chlorohydrin are believed to be 56° (hydrated) and 104° (anhydrous). It is conveniently purified through the Na salt. This salt in H₂O, treated with NaN₃, gave α -triazio- β -hydroxy- β -phenylpropionic acid, lustrous needles, m. 122°; 1 g. is sol. in 4 cc. hot H₂O or 16 cc. hot C₆H₆. Effervescence is very vigorous with coned. H₂SO₄ but very slow with SnCl₄. With Me₂SO₄ in aq. NaOH, the *methoxy derivative* is formed, striated aggregates of prisms, m. 91°; it is more stable towards hot aq. NaOH than the HO deriv.

C. J. WEST

Preparation of sodium and potassium phthalimide. D. L. HAMMICK AND GEO. H. LOCKET. *J. Chem. Soc.* 121, 2362-3 (1922).—Landsberg's method (*Ann.* 215, 181) is unsatisfactory because of the large vols. of solvent needed and because of the presence of H₂O. Working in EtOH with EtONa or EtOK, 50 and 68% of the calcd. yield of the Na and K derivs. were obtained. In AmOH, however, with a hot soln. of 1.5 times the calcd. amt. of Na in AmOH, 91 and 97% of the Na and K derivs. were obtained.

C. J. WEST

Resolution of tropic acid and the stereochemical configuration of the cinchona alkaloids. HAROLD KING AND A. D. PALMER. *J. Chem. Soc.* 121, 2577-86 (1922).—This work was undertaken with the thought that in a closely allied group of alkaloids, like the cinchona group, the stereochem. factor might be of detg. influence on the soly. of the various combinations with *d*- and *l*-tropic acid, so that from the exptl. results one might be able to say with some degree of certainty that certain of the alkaloids were stereochem. related. No light was thrown on the stereochem. factor but the soly. was

shown to be sensitive to other factors, such as the reduction of the vinyl group, the replacement of MeO by EtO, etc. The isolation of *d*-tropic acid is best effected by quinine, hydroquinine and ethylhydrocupreidine being almost as good, while for the isolation of *l*-tropic acid quinidine and ethylhydrocupreine are equally good. *Hydroquinine d-tropate*, obtained in 66% yield, clusters of glistening prismatic needles, m. 184–5°, $[\alpha]_D$ in abs. alc. —83.3°. *Hydroquinidine dl-tropate monohydrate*, clusters of prisms, m. (air-dried) 116–8°, (dried at 100°) 137–9°, $[\alpha]_D$ of hydrate in abs. alc. 137.4°, for anhydrous salt, 142.4°. In some expts. the anhydrous salt was obtained as long, glistening, silky needles, m. 137–9°. *Ethylhydrocupreine l-tropate*, in 60% yield, clusters of small needles, m. 199–200°, $[\alpha]_D$ in abs. alc. —109.3°. *Ethylhydrocupreidine d-tropate*, soft voluminous masses of fine needles, m. 182–3°, $[\alpha]_D$ in abs. alc., 150.7°. The *l-tropate monohydrate* forms clusters of prisms, m. (air-dried) 121–3°, (dried at 100°) 131–3°, $[\alpha]_D$ 118.8° for hydrate, 123.2° for anhydrous salt. *Quinotoxine l-tropate monohydrate*, small cream-colored needles, m. 116–8°; $[\alpha]_D$ for anhydrous salt 8.71°. *Cinchotoxine l-tropate*, fine matted needles, m. 145–6°, $[\alpha]_D$ 10.3°. *Hydrocinchonine d-tropate monohydrate*, large hemispherical tufts of needles, m. (air-dried) 178–95°, $[\alpha]_D$ 116.8°, or for anhydrous salt, 121.3°. Owing to the formation of a complete series of mixed crystals, resolution with cinchonidine is very slow. Repeated crystn. showed that the resolution was in the direction of the *l-tropate*, which was then prepd. from pure materials, fine needles with 1 H₂O, m. 131–3°, $[\alpha]_D$ for the anhydrous salt, —84.3°. The same is true of hydrocinchonidine, the *l-tropate monohydrate* of which forms hemispherical tufts of glistening needles, which soften at 80° and m. 110° and (air dried) m. 130°, $[\alpha]_D$ for hydrate —63.2°, and for anhydrous salt —65.7°. In all cases the tropic acid was recovered and the rotation and m. p. were detd. The optical contribution of the asym. C is discussed and schematically represented. C. J. WEST

Light reactions of the *cis*- and *trans*-cinnamic acids. HANS STOBBER AND F. K. STEINBERGER. *Ber.* 55B, 2225–45 (1922).—S. denies the justice of de Jong's claim to priority in this field (*C. A.* 16, 2683). He and de J. found independently, and apparently simultaneously, that exposure of *cis*-cinnamic acid (A) to sunlight gives, besides the expected β -truxinic acid (B), *trans*-cinnamic (C) and α -truxillic acid (D). Like de J., he believes that 1 mol. D is formed from 2 mols. C but does not agree with de J.'s view that B is formed from 1 mol. each of A and C; it was to clear up this question that the present work was undertaken. Long exposure (96 hrs.) of the liquid melt of A to the rays of a quartz-Hg lamp produces extensive isomerization into C but neither B nor D is formed, the melt thus behaving like C₆H₆ and MeOH solns., and it may be said in general that *illumination of cinnamic acids in the liquid state (solns. or melts) produces isomerization but no polymerization*. The part played by the different rays in the reaction is shown by the following % of A obtained by illuminating C in 0.25 N C₆H₆ soln. (8 cm. from the lamp, with a 4.4 amp. current) in quartz, uvial and ordinary glass which are transparent, to all rays up to the absorption limit of the C₆H₆, to rays up to 271 μ m and to rays up to 320 μ m, resp.; the 1st figures give the length of the illumination: 20 hrs., 9.0, 6.3, 3.2; 62.3 hrs., 22, 16.6, 4.8; 92.5 hrs., —, 18.8, 5.1; 137.5 hrs., 23.5, —, 6.0. *The chief action is therefore to be ascribed to the rays from 270 to 320 μ m, although the shorter and the longer rays are also not without influence.* Below are the length of illumination with the quartz-Hg lamp and the % yields of A, C, D and B, resp., obtained from the solid acids: A (solidified melt), 200 hrs., 60.9, 34.7, —, 4.4; equal parts of A and C (solidified melt), 200 hrs., 39.1, 55.3, 2.7, 2.9; ditto, 360 hrs., 5.6, 87.4, 5.9, 1.1; 1 part A + 2 parts C, 112 hrs., 18.8, 77.2, 4, —; A (finely divided, obtained by evapn. of the Et₂O soln.), 364 hrs., 97.7, 1.6, —, — (loss, 0.7%); equal parts of A and C, 364 hrs., 48.3, 50.9, 0.3 (B + D) (loss, 0.5%); C, 364 hrs., —, 97.6, 2.0 (B + D) (loss, 0.4%). The corresponding data for illumination in sunlight are as

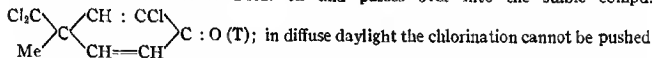
follows: A (powdered), 14 days, 44.6, 37.1, —, 18.3; ditto, 28 days, —, 22.0, 20.1, 50.9; ditto, 17 days, 14.8, 39.2, 14.3, 31.7; equal parts of A and C (pulverized), 17 days, 6.7, 20.2, 54.5, 18.6; A (solidified melt), 20 days, 12.3, 33.4, 21.1, 33.2; equal parts A and C (solidified melt), 20 days, 12.7, 39.3, 30.1, 17.9; A (solidified melt), 27 days, 8.2, 54.0, 4.9, 32.9; A + C (solidified melt), 27 days, 8.1, 48.7, 30.3, 12.9; A (pulverized), 27 days, 6.4, 34.6, 8.7, 50.3; A + C (pulverized), 27 days, 3.5, 24.1, 56.4, 16.0; C (pulverized), 23 days, —, 14.3, 85.7, —. The isomerization reaction proceeds in the same way in both the Hg light and in sunlight, but the yield of dimers is very different in the 2 kinds of light. Taking each day of exposure to sunlight as equal to 7 hrs., A after 200 hrs. in the Hg light gives 4.4% dimers and after 196 hrs. in sunlight 71.0%; for C the values are 2% after 364 hrs. in Hg light and 85.7% after 161 hrs. in sunlight. Long ultra-violet rays favor the polymerization, while short ultra-violet rays hinder it; as will be shown shortly in detail they exert a depolymerizing action on the truxillic and truxinic acids. Comparison of these sunlight expts. in Leipzig with those of de J. in Buitenzorg (*C. A.* 6, 2746) and of Stoermer in Rostock (*C. A.* 14, 58) shows that in these various places and under different light conditions A yields B always and generally in predominant amt. but that, especially on long illumination, there is also isomerization into C and subsequent polymerization to D. C, on the other hand, is almost exclusively polymerized to D; only on long illumination are there formed relatively small amts. of B, accompanied with considerable resinification. The expts. with mixts. of equal parts of A and C show that the C mixed with the A produces no increase of B, and that therefore, contrary to de J.'s belief, B is formed only from 2 mols. A, and, in agreement with Stoermer and Scholtz (*C. A.* 15, 1888), Stobbe and Steinberger conclude that B has a meso and not the racemic structure assigned to it by de J. Expts. by Stobbe and Lehfeldt have shown that β -arylacrylic acids (including C) are dimerized and autoxidized to BzH, both in the solid state and in aq. suspension; both processes are accelerated by a few drops of HCl (the oxidation more than the dimerization) and on long illumination the yield of D diminishes and that of BzH increases. A behaves similarly, the yield of B on long illumination, especially in the presence of HCl, decreasing as the result of autoxidation of the A. Below are the % of C, D, B and resin, resp., on exposure to sunlight in HCl suspension: A, 9 days, 53.9, —, 38.2, 7.9; A + C, 9 days, 58.4, 18.1, 18.4, 5.1; A, 20 days, 53.53, 0.33, 38.13, 8.01; A + C, 20 days, 55.6, 21.7, 15.7, 7.0. In all the expts. a strong odor of BzH developed. Here, too, contrary to de J.'s hypothesis, the formation of B is independent of the presence of admixed C; both isomers polymerize, even in suspension, independently to their dimers. When the acid freshly prepd. from the Na salt of C is illuminated in sunlight in HCl suspension, it unexpectedly yields only B (37.5%, together with 5% C and 57.5% BzH and resin after 5 months) and no D, whence the acid being illuminated, at least at the beginning of the expt., must have been exclusively the metastable β -form of C. This does not justify de J.'s conclusions that "the *trans*-acid can give B and D," and that "the formation of B from A proceeds not directly but indirectly through the *trans*-acid." A more plausible assumption is that the very reactive β -*trans*-acid isomerizes more rapidly than C into A, which then polymerizes normally to B. As the reaction occurs in the solid crystals, not in isotropic solns. or melts, this difference in the velocity of reaction of the α - and β -forms of C is no evidence that the 2 substances are chemically isomeric; they may just as well be the 2 forms of a dimorphous compd. The increase in the yield of D from A with increase in temp. is not conditioned by the increase in the temp. alone, as assumed by de J., but chiefly by the fact that the A liquefies above 60° and that, as shown above, the A in liquid form easily isomerizes into C.

C. A. R.

Transformation products of 1-methyl-1-trichloromethylcyclohexa-2,5-dien-4-one. K. v. AUWERS AND W. JÜLICHER. *Ber.* 55B, 2167-91(1922).—The uncompleted in-

vestigation of Zincke on the above ketone (A) (*C. A.* 2, 1701) has been continued, with his coöperation (unpublished results by Z. and Nassauer are included in this paper), for purposes of comparison with the 1-CHCl₂ ketone (B) (*C. A.* 1, 2096). In addition to the oxime and phenylhydrazone prepd. by Z. and Suhl it yields a semicarbazone and a *p*-nitrophenylhydrazone. While A and most of its transformation products undergo a deep-seated change with H₂SO₄ in the cold or on gentle warming, the oxime is not attacked even at 120°; this resistance to acids probably explains the failure to rearrange the oxime by the method of Beckmann and Wallach; PCl₅ in Et₂O gives a substance, m. 180–2°, contg. P, whose investigation did not seem promising. On A itself PCl₅ acts as on B, giving through the labile intermediate product Me(Cl₂C) : C₆H₄ : Cl₂ (C) the compd. 3,4-Me(Cl₂C)C₆H₃Cl (D); these substances were not purified but the formation of the end product was proved by converting it into 2,4-MeC(Cl₂C)₂H (E), m. 166–7°. The series of reactions typical of B and its analogs, whereby semibenzene derivs. are obtained by converting the ketones with Grignard reagents into tert. carbinols and then cautiously splitting off 1 mol. H₂O (by mol. rearrangement these semibenzene derivs. finally pass over into true aromatic compds.), also applies to A, as already shown by Z. and Schwabe, although they were not able to isolate the labile semibenzene deriv. as such. The carbinol Me(Cl₂C) : C₆H₄ : (OH)Me (F), m. 131–2°, as a rule changes after a few hrs., with violent ebullition and loss of H₂O, into a C₆H₅ deriv. *p*-MeC₆H₄CH₂CCl₃ (G), but it has been found that its stability depends largely on the way in which it is kept; in an evacuated desiccator a sample remained completely unchanged for 24 hrs. and in a CO₂ atm. it began to lose H₂O only after several weeks, it is apparently the acid lab. air, above all, which rapidly decomps. it. From F kept several hrs. in ice, Z. and Schwabe obtained the pure G but as, during the long interval, the labile intermediate product Me(Cl₂C) : C₆H₄ : CH₂ (H) had completely rearranged or otherwise changed they were unable to isolate it. Attempts to prep. H by the action of cold HCO₂H on F gave an impure product, not only H₂O but HCl also being split off. H can be satisfactorily prepd., however, by passing H through a gently warmed suspension of the pure F in petr. ether. Although the elimination of HCl cannot be completely avoided even by this method, the compn. and optical consts. of the product show that it is approx. pure. It is immediately oxidized by cold KMnO₄ and rearranges at a slightly elevated temp. into the isomeric G. Besides the purity of the F from which it is prepd., the way in which it is kept largely influences its stability; a sample in a tightly closed flask filled with air decompd. so violently after a short time that the flask was shattered, while in a CO₂ atm. it polymerized only gradually. D is obtained more rapidly than by Z. and Schwabe's method by warming F or H in much AcOH on the H₂O bath; boiling alc. alkalis convert it into the styrene *p*-MeC₆H₄CH : CCl₂ (I), which is oxidized to *p*-MeC₆H₄CO₂H. The 4-Ph analog (J) of F, from A and PhMgBr, loses H₂O less easily than F, the crystals beginning to become sirney only after weeks, even when no special precautions are taken to protect them. Conc'd. HCO₂H eliminates H₂O from it, yielding an exceedingly unstable oil, which immediately after its prepn. begins to evolve HCl and in a few hrs. solidifies to a glassy sticky mass which on distn. *in vacuo* evolves HCl in abundance and yields only a small amt. of *q*-ethyl β -phenyl (K), formed by reduction of the expected dehydration product, also obtained by condensation of Ph₂ with AcCl by the Friedel-Crafts method and reduction of the resulting ketone by the Clemmensen method. The course of the dehydration and further conversion of J therefore differs characteristically from that of F but in both cases it is the CCl₂ group which migrates. Attempts to bring about a reaction between A, Zn and BrCH₂CO₂Et in C₆H₆ met with considerable difficulty until it was discovered that the C₆H₅ had to be completely freed of S impurities by boiling with AlCl₃. The primary product of the reaction, Me(Cl₂C) : C₆H₄ : (OH)CH₂CO₂Et (L), passes over on gentle

warming or shaking with concd. HCO_2H into the ester $\text{Me}(\text{Cl}_3\text{C}) : \text{C}_6\text{H}_4 : \text{CHCO}_2\text{Et}$ (M) and then rearranges, with violent ebullition, into the ester $p\text{-MeC}_6\text{H}_4\text{CH}(\text{CCl}_3)\text{CO}_2\text{Et}$ (N), which is always obtained when it is attempted to sapon. M to the free acid. The structure of the free acid of N is proved by conversion into $p\text{-MeC}_6\text{H}_4\text{C}(:\text{CCl}_3)\text{CO}_2\text{H}$ (O) and oxidation of the latter to $p\text{-MeC}_6\text{H}_4\text{CO}_2\text{H}$. With concd. H_2SO_4 , L gives an acid (P), probably 2,4- or possibly 3,4- $\text{Me}(\text{HO}_2\text{CCH}_2)\text{C}_6\text{H}_3\text{CO}_2\text{H}$, oxidized by KMnO_4 to an acid agreeing, in the way it melts, with methylterephthalic acid. Under the same conditions F gives 2,4- $\text{Me}_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$ (Q), m., $125-6^\circ$ which is oxidized to 2,1,4- $\text{C}_6\text{H}_3\text{Me}(\text{CO}_2\text{H})_2$, m. $323-5^\circ$ (di-Me ester, m. $70-3^\circ$). J gives the acid 2,4-Me- $\text{PhC}_6\text{H}_3\text{CO}_2\text{H}$ (R), oxidized to 4,1,2- $\text{C}_6\text{H}_3\text{Ph}(\text{CO}_2\text{H})_2$ (S) which loses H_2O on fusion and is converted into its anhydride with the greatest ease by AcCl . The Ca salt of R, distd. with an excess of lime, gives $m\text{-MeC}_6\text{H}_4\text{Ph}$, b. $272-4^\circ$, which is oxidized by alk. KMnO_4 to $m\text{-PhC}_6\text{H}_4\text{CO}_2\text{H}$, m. 161° . Treated in CCl_4 for several hours with Cl in the presence of I, A absorbs 1 mol. Cl but the resulting dichloride at once begins to give off HCl when the solvent is distd. off and passes over into the stable compd.



further but in strong sunlight there is obtained the stable tetra-Cl addn. product $\text{Me}(\text{Cl}_3\text{C})\text{C}(\text{CHCl}_2\text{CHCl}_2)\text{C} : \text{O}$ (U), which passes over into the di-Cl substitution product, $\text{Me}(\text{Cl}_3\text{C})\text{C}(\text{CH} : \text{CCl}_2)\text{C} : \text{O}$ (V), only on treatment with alkali. The prepn. and properties of the compd. m. $171-3^\circ$ (W) obtained by Schwabe by the bromination of A leave no doubt that it has the structure $\text{Me}(\text{Cl}_3\text{C})\text{C}(\text{CH} : \text{CBr}_2)\text{C} : \text{O}$ assigned to it by S. With MeMgBr in C_6H_6 W yields the carbinol $\text{Me}(\text{Cl}_3\text{C})\text{C}(\text{CH} : \text{CBr}_2)\text{C}(\text{OH})\text{Me}$ (X) (its indefinite m. p. suggests that it may consist of a mixt. of stereoisomers), which loses H_2O (and rearranges simultaneously) only at high temps. and is hardly attacked by cold concd. HCO_2H ; when, however, it is heated with HCO_2H , it yields the compd. $\text{Me}(\text{Cl}_3\text{C})\text{C}(\text{CH} : \text{CBr}_2)\text{C} : \text{CH}_2$ (Z) which, unlike the isomer (Y) obtained by Z. and Schwabe by brominating F, decolorizes cold KMnO_4 and foams energetically on fusion. Y must therefore have the structure $p\text{-MeC}_6\text{H}_4\text{CBr}_2\text{CCl}_3$; it cannot be rearranged by heating to high temps. or by other means, is indifferent towards KMnO_4 and is characterized by its great stability; for this reason it cannot be converted into $p\text{-MeC}_6\text{H}_4\text{COCO}_2\text{H}$ or $\text{MeC}_6\text{H}_4\text{CO}_2\text{H}$ by long boiling with alc. KOH, and attempts to synthesize it from PhMe and CCl_3COCl with subsequent treatment of the expected ketone with PCl_3Br_2 failed owing to the instability of the 1st product. On the whole, A and B behave alike in all essential points; especially characteristic of both types of compds. is their tendency to pass over, directly or indirectly, into aromatic compds., by migration in some cases of the Me, in others of the CCl_3 (or CHCl_2) group, depending on the nature of the rearranging agent and of the rearranging substance. *Semicarbazone* of A, needles from alc., m. $197-8^\circ$; *p*-nitrophenylhydrazones, yellow tables from dil. AcOH, m. $159-60^\circ$. 1-Methyl-1-trichloromethyl-4-methene-2,5-cyclohexadiene (H) (found Cl, 46.8; calcd., 47.6%), light yellow oil, $d_4^{19.5} 1.2022$, $n_D^{19.5} 1.55171$, 1.55710 , 1.56986 for α , D and β at 19.5° , M 59.38 , 59.86 and 1.61 , $E_D^{2.22} 2.28$ and 39% for α , D and β - α , resp. 1-Methyl-1-trichloromethyl-4-phenylcyclohexa-2,5-dien-4-ol (J), stout needles from MeOH or heavy benzene, m. $120-1^\circ$ (yield, 20 g. from 20 g. A). K, tables with fatty luster from dil. MeOH, m. $46-7^\circ$ (that the $\text{PhC}_6\text{H}_4\text{Ac}$ prepd. for the synthesis of K by condensing AcCl with PhI is the *p*- and not the *m*-compd. as believed by Adam (*Ann. chim.* [6] 15, 255(1888)) is shown by the fact that it is oxidized by CrO_2AcOH on the H_2O bath to $p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$). 2-Methyl-4-phenylbenzoic acid (R) (in its prepn., to avoid sulfonation the J is not added to concd. H_2SO_4 but is treated dropwise in 10 parts AcOH with 8 parts H_2SO_4), leaflets from benzene, m. $169-70^\circ$; silver salt, fine leaflets; methyl ester, leaflets from MeOH, m. $61-3^\circ$. The *m*-methylphenyl obtained by distg. the Ca

salt of R with lime shows d_4^{25} 1.0182, n_D^{25} 1.59747, 1.60443, 1.62386 for α , D and β at 16.7°, M 56.29, 56.82, 1.99, E_D 1.01, 1.07 and 40% for α , D and β - α , resp. *Diphenyl-3,4-dicarboxylic acid* (S), from R with hot alk. $KMnO_4$, m. 194°; *anhydride*, needles from C_6H_6 , m. 135–6°. *1-Methyl-1-trichloromethylcyclohexa-2,5-dien-4-ol-4-acetic acid*, from 20 g. A, 18 g. $BrCH_2CO_2Et$ and 6.6 g. Zn shavings (etched with H_2SO_4 and dried) refluxed 3 hrs. in 20 g. C_6H_6 , the resulting crude dark oily ester (L) being sapond. by letting it stand 12 hrs. in the cold with 2 mols. alc. KOH, fine needles from C_6H_6 , m. 125–6° (decompn.). *Methyl-1-methyl-1-trichloromethylcyclohexa-2,5-diene-4-methene-carboxylate* (M), dark brown oil, cannot be completely freed from accompanying A nor sapond. to the free acid. α -*p-Tolyl- β,β,β -trichloropropionic acid*, best prepd. by cautiously heating the above HO acid on the H_2O bath, tables from CaH_2 , m. 108.5–9.5°. *p-Methyl- β,β -dichlorotartaric acid* (O), from any of the 3 preceding compds. vigorously treated with alc. KOH (best obtained by boiling the HO acid 0.5 hr. with 10 parts concd. alc. KOH), fine needles from dil. $AcOH$, m. 118.5–20°. *1-Methyl-2-carboxybenzene-5-acetic acid* (P), from the HO acid in 15–20 parts cold concd. H_2SO_4 , needles from H_2O , m. 198.5–9.5°. *1-Methyl-1-trichloromethyl-3-chlorocyclohexa-2,5-dien-4-one* (T), needles from $MeOH$, m. 99°; *oxime*, needles from heavy benzene, m. 162–4°; *p-nitrophenylhydrazone*, yellow needles from CaH_2 , m. 146–8°. *1-Methyl-1-trichloromethyl-2,3,5,6-tetrachloro-4-cyclohexanone* (U), needles from heavy benzene, m. 134–6°, remained unchanged for a year and is therefore probably the stable *trans*-form, converted by treating in boiling alc. with NaOH to distinct alkyl. into *1-methyl-1-trichloromethyl-3,5-dichlorocyclohexa-2,5-dien-4-one* (V), tables from heavy benzene, m. 161–2°. W, thick tables or stout needles from heavy benzene, m. 172°, is obtained in good yield from A allowed to stand 1 day in an excess of Br in bright sunlight and evapd. on the H_2O bath or by gently warming the soln. after adding a little I. *1,4-Dimethyl-1-trichloromethyl-3,5-dibromocyclohexa-2,5-dien-4-ol* (X), needles from heavy benzene, softens 88°, m. 90–2° (clear, 95°). *1-Methyl-1-trichloromethyl-3,5-dibromo-4-methene-2,5-cyclohexadiene* (Z), softens 83°, m. turbid 90°, rearranges 100° (foaming). The compd. $Me(Cl_3C) : C_6H_4 : (CBr_3)Br$ m. 140–1° (Z. and S. give 133°). Y, flat needles from $MeOH$, m. 90–1°, is best obtained by fusing the preceding compd. C. A. R.

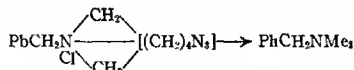
Action of the chlorides of phosphorus on chlorodimethyldihydroresorcinol. L. E. HINKLE AND WM. D. WILLIAMS. *J. Chem. Soc.* 121, 2498–502 (1922); cf. Crossley and Le Sueur, *J. Chem. Soc.* 83, 113.—Neither PCl_3 nor $POCl_3$ has any appreciable action on chlorodimethyldihydroresorcinol (A). The action of 1.5 mols. PCl_3 on 1 mol. A in $CHCl_3$ (4 hrs. on the H_2O bath) gave as the primary product a tri-Cl deriv., which readily loses HCl, yielding *4,5-dichloro-1,1-dimethyl- Δ^2 -cyclohexen-3-one*, prisms, m. 63°. It does not combine with Cl in cold or hot $CHCl_3$ but substitution takes place slowly with Br in hot $CHCl_3$. Heated with concd. H_2SO_4 at 120°, A is formed, HCl being evolved. The other products of the reaction are *3,4,5-Cl₃C₆HMe₂*, *3,4,5,6-Cl₄C₆Me₂*, a *monochloroxylenol* (B), slender crystals, m. 80–1°, and a *xylenol*, m. 162–3°, which was not further investigated. B yields a *benzoate*, m. 86°, and a *trichloroxylenol* m. 181°. C. J. WEST

Preparation of the *d*-pimaric acid of melting point 212°. EDMUND KNECHT AND EVA HUBBERT. *J. Soc. Dyers Colourists* 38, 221–2, 265 (1922).—Dissolve 26 g. *d*-pimaric acid in a slight excess of NaOH soln. over that required to form the Na salt. Dil. to 2.5 l. and add 400 cc. NaOCl soln. contg. 27.5 g. available Cl per l. Let stand overnight for crystals to settle. Wash by decantation, filter, dissolve in boiling H_2O and decomp. with dil. H_2SO_4 . Purify by recrystn. from alc. Yield, about 10%.

CHAS. E. MULLIN

Tertiary amine derivatives of benzohydril-amine. MARCEL SOMMELET. *Compt. rend.* 175, 1149–51 (1922).—Tertiary amines contg. the group NMe_3 were prepd.

(C. A. 16, 1930) by warming quaternary salts of hexamethylenetetramine (A) with HCO_2H , the acid decomp. into H_2 and CO_2 and the H_2 was absorbed. The reaction



was applied to analogs of A, among them condensation products of A with Ph_2CHBr , and under the influence of HCO_2H dimethylbenzohydrylamine (B) is formed, crystals, m. 68.5–70.5°; the hydrochloride m. 201–1.5°; hydroiodide (D) m. 227–8°; hydrobromide (E), m. 199–200°. B is identical with the product formed from Pb_2CHBr and Me_2NH in C_6H_6 . B combines with MeI in MeOH much more slowly than the bases of the $\text{PhCH}_2\text{NMe}_2$ group. The addn. is effected slowly in the cold. The methiodide (F), $\text{Ph}_2\text{CHNMe}_3\text{I}$, needles, m. 211°, was prepd. in the cold but more rapidly when heated but is contaminated then by D. Diethylbenzohydrylamine, m. 58–9°, benzohydryl-piperidine, m. 73–4°, and ethylbenzylbenzohydrylamine m. 65–6°, were also prepd. When these amines in MeOH are subjected to the action of MeI at 100° the hydroiodides are produced. When MeBr is used, the hydrobromides are formed. The insol. methiodides and methobromides were not formed, but a gas was evolved and an oily compd. was formed. The action of MeBr on B in MeOH at 100° during 48 hrs. in sealed tubes resulted in the formation Me_2O , Ph_2CHOMe and Me_2NHBr . In BuOH, Me_2O , Bu_2O , and Ph_2CHOBu were formed. $\text{MeBr} + \text{MeOH} + \text{B} = \text{Me}_2\text{O} + \text{Ph}_2\text{CHNMe}_2\text{HBr}$. The Me_2O results from the interaction of MeBr and MeOH, and the HBr then interacts with B. Simultaneously the methobromide of B dissociates. $\text{Ph}_2\text{CHNMe}_2\text{Br} = \text{Ph}_2\text{CHBr} + \text{Me}_2\text{N}$; $\text{Ph}_2\text{CHBr} + \text{MeOH} + \text{Me}_2\text{N} = \text{Ph}_2\text{CHOMe} + \text{Me}_2\text{NHBr}$. When F or E is subjected to the action of MeOH at 100°, Ph_2CHOMe is formed and in the case of F also Me_2NHBr and of E, Me_2HNHBr . H. E. WILLIAMS

Dyes derived from saccharin. The sulfamphthaleins. SIKHIBHUSHAN DUTT. J. Chem. Soc. 121, 2389–91(1922).—The difficulty of obtaining pure o- $\text{HO}_2\text{SC}_6\text{H}_4\text{CO}_2\text{H}$ led to an investigation of the action of saccharin (A) on amines and phenols. The condensation products are characterized by their color and fluorescence and closely resemble the corresponding phthalcins. A, PhOH and H_2SO_4 at 100–10° for 10 hrs., gave in 15% yield phenolsulfamphthalein, $\text{C}_{20}\text{H}_{14}(\text{C}_6\text{H}_4\text{OH})_2\text{NH}_2\text{SO}_2$, yellow prisms, be-

coming red on rubbing. The yellow form is the more unstable. The alk. soln. is pink, the aq., AcOH or alc. soln. yellow. Trisodium salt, dark red, extremely hygroscopic substance; trimethyl derivative, needles, m. 142°. Dibenzoate silky needles, m. 127°. Diacetate, needles, m. 112°. Resorcinolsulfamphthalein, using ZnCl_2 as the condensing agent, brownish yellow microneedles, sol. in alkali with an orange color, which, on diln., shows a very intense yellowish green fluorescence. The Na salt dyes light yellow shades on wool. Orcinolsulfamphthalein, brownish yellow needles, sol. in alkali with blood-red color, showing on diln. a brilliant green fluorescence. The Na salt dyes pink shades on wool. Phloroglucinolsulfamphthalein, long, brownish yellow needles, sol. in alkali with an orange-red color but the soln. shows no fluorescence. The Na salt dyes fine orange shades on wool. Hydroxyquinolsulfamphthalein, light, reddish brown silky needles, sol. in alkali with a pink color, which shows a feeble yellow fluorescence. The acetate forms colorless prisms, m. above 300°. The Na salt dyes pink shades on wool. Catecholsulfamphthalein, brown microneedles, sol. in alkali with a green color. 1,2,4,5-Tetrahydroxybenzenesulfamphthalein, dark brown needles with green metallic luster; the alk. soln. has a pink color but no fluorescence. The hexaacetate forms silky needles, m. above 290°. 4,4'-Diamino-2,2'-iminophenylsulfamphthalein, from A and m- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, bright yellow prismatic needles, whose soln. shows an intense yellow-green fluorescence. A by-product of this reaction is a compound, $\text{C}_{20}\text{H}_{12}\text{O}_8\text{N}_2\text{S}_2$, brown

needles which also exhibits green fluorescence in soln. With boiling alkali it yields A and the above dye. 2,2'-Iminophenolsulfamphthalein, from A and $m\text{-HOC}_6\text{H}_4\text{NH}_2$, purified through the Pb lake, dark brown, sol. in alkali with a brown color but no fluorescence, though in EtOH and AcOH there is a fine moss-green fluorescence. A, $m\text{-Me}_2\text{NC}_6\text{H}_4\text{OH}_2$ and ZnCl_2 give 4,4'-tetramethyldiamino-2,2'-oxidodiphenylsulfamphthalein, small pink needles with golden luster, sol. in dil. mineral acids with pink color and strong yellow fluorescence. The substance $\text{C}_{22}\text{H}_{22}\text{O}_2\text{N}_2\text{S}_2$ results from A, 1,3,4,6-(HO)- $\text{C}_6\text{H}_3(\text{NH}_2)_2$ and ZnCl_2 at 160° for 3 hrs., dark brown amorphous product, sol. in alkali with blue color but no fluorescence.

C. J. WEST

2,4-Dinitrobenzil. GERALD BISHOP AND O. L. BRADY. *J. Chem. Soc.* **121**, 2364-70 (1922).—The unsym. benzils are of interest because of the peculiarities often associated with such compds. and the possibilities of isomerism among their derivs. The unsym. substituted stilbenes were used as starting material, but it was found that the addn. of Br took place very slowly if more than 2 NO_2 groups were present in one ring. 2,4-(O_2N) $\text{C}_6\text{H}_3\text{CH}:\text{CHPh}$ was prepd. by condensing 2,4-(O_2N) $\text{C}_6\text{H}_3\text{Me}$ and BzH in C_6H_6 , 1 cc. $\text{C}_2\text{H}_5\text{N}$ being added at the start and after boiling 6 hrs.; yield, 60%. The 2,4,6-(NO_2) $_3$ deriv. was obtained in 80% yield. 2,4,6,2'-Tetranitrostilbene, glistening, light brown needles, m. 181° . 2,4,6,3'-Tetranitrostilbene, lemon-yellow leaflets, m. 159° . Bromination and boiling with AcOAg in AcOH gave monoacetyl-2,4-dinitrohydrobenzoin, large, irregular, lemon-yellow crystals, m. 182° . Hydrolysis with 20% EtOH- H_2SO_4 gave 2,4-dinitrohydrobenzoin, powder, m. 148° . Heating on the H_2O bath with 4 parts by wt. of HNO_3 for about 6 hrs. gave 2,4-dinitrobenzil (A), canary-yellow rectangular plates, m. 105° , the yield being about 30%. The α -monoxime, (O_2N) $_2\text{C}_6\text{H}_3\text{COC}(\text{NOH})\text{Ph}$, is obtained by heating A in alc. with $\text{NH}_2\text{OH}\cdot\text{HCl}$ for 2 hrs., pearly leaflets, m. 181° . Its configuration was established by the formation of 2,4-(O_2N) $_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$ and BzCN upon treatment with PCl_5 (intermediate chloro compound, $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2\text{Cl}$, powder) and shaking the Et_2O soln. with dil. NaOH . The action of 2 N NaOH on the H_2O bath gave BzH and 2,4-(O_2N) $_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$. The β oxime, (O_2N) $_2\text{C}_6\text{H}_3\text{C}(\text{NOH})\text{COPh}$, results when an ice-cold soln. of A in alc. is shaken with free NH_2OH , micropowder, m. 159° . Upon treatment with PCl_5 and NaOH , this yields BzOH and 2,4-(O_2N) $_2\text{C}_6\text{H}_3\text{NH}_2$, thus establishing its constitution. This is more readily attacked by 2 N NaOH and yields 2,4-(HO)(O_2N) $\text{C}_6\text{H}_3\text{CN}$ and BzOH . Phenylhydrazones, orange-red needles, m. 210° . Semicarbazone, cryst. powder, m. 215° . The configuration of these compds. has not yet been detd.

C. J. WEST

Triphenylmethyl. XXXI. Tautomerism of *o*-hydroxytriphenylcarbinol; *o*-hydroxy- and alkyloxytriphenylmethyl. M. COMBERG AND D. NISHIDA. *J. Am. Chem. Soc.* **45**, 190-207 (1923); cf. *C. A.* **16**, 3179.— $p\text{-HOC}_6\text{H}_4\text{CPh}_2\text{OH}$ and many of its analogs are prone to tautomerize and, on heating, yield *p*-fuchsones. The 2 tautomeric carbinols have been actually isolated in a no. of cases. The corresponding carbinol chlorides have an even greater tendency towards quinoidation and, in fact, the benzenoid form may be considered as non-existent. However, the quinonoid chlorides themselves are also extremely unstable and dissociate very readily, both in soln. and in solid form, into fuchsones and HCl , so that it is not possible to prep. the radical $p\text{-HOC}_6\text{H}_4\text{CPh}_2$. The *o*-HO compd. and some of its ethers have now been examd. from the same 2 points of view, viz., as regards their tendency to tautomerize and the possibility of prep. the triaryl methyl radicals. Solns. of $o\text{-HOC}_6\text{H}_4\text{CPh}_2\text{OH}$ (A) in AcOH , CCl_4 , C_6H_6 , PbMe , xylene or PhBr when heated begin to become brown at $50\text{--}80^\circ$, depending on the solvent; the intensity of the color increases with the temp. and with the concn. of the A; on cooling the color gradually decreases and disappears at the same temp. as that at which it began to appear. The color change is reversible at any temp. below 110° and the A is quant. recoverable. The AmOH , $\text{C}_6\text{H}_5\text{N}$, PhNH_2 and PhNO_2 solns. remain colorless.

The tautomerization is greatly hindered by small and completely prevented by larger amts. of H_2O , while dehydrating agents (up to 50% of Ac_2O in $AcOH$) seem to have no pronounced influence on the process. Above 110° A slowly loses H_2O ; the product is not the fuchsone, however, but its colorless rearrangement product, 9-phenylxanthane (B), m. $144-5^\circ$. The tautomerization of A occurs not only in soln. but also in the dry state; the A turns brown at 100° and at 110° (30° below its m. p.) begins to lose H_2O with formation of B. Apparently the quinonoid tautomer exists only at elevated temps., up to 110° , when it passes into the fuchsone, which is unstable and rearranges into B. $o-HOC_6H_4CPh_2Cl$ (C), when fresh, is a white cryst. compd. but at once begins to lose HCl and becomes brown, slowly even below 10° (both in the solid state and in soln.); below 65° it forms a dark brown jelly-like substance; above 65° the main product of the decompn. is B. The jelly-like substance is probably a polymerized fuchsone; heated with $AcOH$, it gives B. C, being much more stable than the *p*-isomer, actually gives, with metals, the triarylmethyl; this, however, could not be isolated because the C partly decomp., as stated above, with liberation of HCl , which catalytically converts any of the triarylmethyl formed into the stable polymeric benzokynyltetraphenylmethane derivative (D), crystals from CS_2-Me_2CO , m. 237° . If the C is shaken with mol. Ag in CS_2 in the presence of O, there is formed, in addn. to D, the peroxide, m. 131° , sol. in warm alkalis. *o*-Benzoyloxytriphenylcarbinol (17.6 g. from 14 g. A in 60 cc. of *N* NaOH heated with 9 g. $PhCH_2Cl$), m. 172° ; 18 g. in C_6H_6 and $CaCl_2$ satd. with HCl gives 17.5 g. of the chloride (E), m. 146° , which, although considerably more stable than C, gradually decomp. spontaneously even at room temp., into HCl , BzH and the

$$\begin{array}{c} CPh_2- \\ | \\ \text{unsatd. hydrocarbon} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \end{array}$$

which instantly changes into a polymer, light yellow

powder from $Et_4O-EtOH$, m. $126-9^\circ$. With Ag, E behaves like C; peroxide, m. 153° ; polymer, m. 207° . $o-PhOC_6H_4CPh_2OH$ when treated in C_6H_6 does not give the chloride but 9,9-diphenylxanthene. *o*-Acetoxytriphenylcarbinol, from A boiled with Ac_2O and $NaOAc$, m. 246° , gives no color when boiled with $AcOH$; with HCl in Et_2O it loses the Ac group and yields C. $o-MeOC_6H_4CPh_2OH$, prepd. by the Grignard method from Ph_2CO and $o-MeOC_6H_4I$, $lit.$ m. $150-5^\circ$, gives with HCl in C_6H_6 in the presence of $CaCl_2$ 94% of the chloride, which does not lose HCl or $MeCl$ even when heated up to 130° ; bromide, m. $127-8^\circ$ (yield, 90%). Shaken 12 hrs. in 100 cc. CS_2 with 5 g. mol. Ag, siphoned off from the Ag, concd. to 10 cc. and treated with an equal vol. of petr. ether, 5 g. of the chloride yields 2-3 g. *o*-methoxytriphenylmethyl (F) (naturally in equil. with its association product, *di*-*o*-methoxyhexaphenylethane (G)), crystals which are almost colorless at first but become light yellow on drying, m. $117-21^\circ$, forms dark reddish orange solns. which rapidly absorb nearly the calcd. amt. of O but yield only about 82% of the peroxide, m. $160-1^\circ$ (decompn.). F in C_6H_6 absorbs about 65% of the calcd. amt. of I; the resulting iodide was not isolated but its presence in the soln. was established by converting it into the aniline deriv., $MeOC_6H_4CPh_2NHPh$, m. 153° . Mol. wt. detns. on G in freezing C_6H_6 (5°), *p*- BrC_6H_4Me (27°) and *p*- $C_6H_4Cl_2$ (53°) showed av. dissociations of 25.8, 32.4 and 49.3%, resp. Using the app. described in an earlier paper to det. the no. of times the colored soln. of G can be decolorized with O and the amt. of O absorbed in each operation, C. and N. find that only about 0.1 of the G in soln. exists as the colored compd. and as the dissociation, as detd. by the f. p. method, is 30%, it is obvious that only about $1/3$ of the total amt. of the monomol. free F is colored and the other $2/3$ is present in the colorless benzenoid form. The mol. cond. in liquid SO_2 at about -10° of the chloride ranges from 102.7 for V 991.5 to 63.6 for V

21.4; of the bromide, from 153.8 for V 1196.0 to 84.6 for V 35.5; of F , from 15.0 for V 1173.0 to 5.1 for V 76.7. XXXII. *p*-Benzyloxy- and *p*-methoxytriphenylmethyl. M. GOMBERG AND C. C. BUCHLER. *Ibid* 207-22.—By blocking the HO group of *p*-HOC₆H₄CPh₃Cl with the heavy group PhCH₂, G. and B. finally succeeded in isolating a free radical, *p*-benzyloxytriphenylmethyl (A), contg. O in the *p*-position to the central C atom. Renewed attempts to isolate *p*-methoxytriphenylmethyl (B) also ended in success. Both A and B are practically colorless or light yellow when fresh but the solns. in org. solvents are always orange-yellow and are rapidly decolorized in the air, with the absorption of the amt. of O calcd. for the formation of the peroxides. C₆H₆ solns. absorb I rapidly, equil. with the iodide being established when 55-60% of the calcd. amt. of I has been absorbed. The radicals react in C₆H₆ with HCl, forming to the extent of 80-95% the chloride and the triarylmethane which only partially interact to form a stable polymer of the free radical. C₆H₆ solns. in quartz test-tubes in direct sunlight become colorless after several hrs., 2/3 of the original free radical being transformed

into a dehydrogenated triarylmethyl (C), $\text{PhC} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4\text{OX} \end{array}$, and the other 1/3 reduced

to the triarylmethane; in the air the solu. absorbs O with formation of the peroxide (D) of C, whose structure was proved by its synthesis from 3-methoxy-9-fluorenone (E), as described below. A and B were recrystd. from a large no. of solvents (esters, ethers, ketones and hydrocarbons), but only 1 additive compd. (between Et₂O and A) was obtained, and only partially, the isolated A never contg. more than 50% of this additive product. *o*-Benzyloxytriphenylcarbinol, obtained in 90% yield from the HO compd. in 2.4 mols. of 10% NaOH heated 4 hrs. at 50° with 1.2 mols. PhCH₂Cl under a reflux with rapid stirring, m. 94°, reduced quant. by Zn dust in boiling AcOH to the methane, needles from alc., m. 116.5°. Chloride, from the carbinol in C₆H₆ with HCl and CaCl₂, m. 77°, gives in C₆H₆ with FeCl₃, ZnCl₂, HgCl₂ or SnCl₄ in AcOEt the corresponding red double salts as oils which later cryst. (except that of Zn). Ethyl ether, from the chloride and NaOEt, fine needles from alc., m. 89°. Bromide, from the carbinol in C₆H₆ and slightly more than the calcd. amt. of AcBr, needles from Et₂O, m. 90°. A, obtained in about 1.5 g. yield from 3 g. of the chloride and 3 g. Ag shaken 8 hrs. in C₆H₆, siphoned off from the Ag, evapd. *in vacuo* at 45-50° and crystd. from Me₂CO, darkens in CO₂ at about 125°, m. 142-5°. Peroxide, obtained in only about 90% yield, although the calcd. amt. of O is absorbed in about 5 min., m. 171°. The iodide was not isolated; the C₆H₆ soln. immediately darkens in the air with liberation of I. Dissociation of the *di-p*-benzyloxyhexaphenylethane in various solvents at their f. p. (the first figure gives the % concn. of the soln., the second the % dissociation): ClCH₂CH₂Br (-17°) 1.30, 48.1; 4.95, 28.5. C₆H₆ (4.9°) 1.31, 41.2; 4.53, 26.7. PhNO₂ (5.8°) 1.12, 35.6; 4.39, 27.1. (CH₂Br)₂ (9.6°) 1.36, 46.1; 4.97, 36.7. *p*-BrC₆H₄Me (27°) 1.17, 39.9; 4.85, 22.5. *p*-C₆H₄Cl₂ (53°) 1.36, 55.9; 5.02, 47.7. *p*-MeOC₆H₄CPh₂OH, m. 82°, is obtained in 80-95% yield from 44 g. of the HO compd. in 1.6 mols. of 10% NaOH treated in the course of 1 hr. with 1.3 mols. Me₂SO; warmed in Et₂O with 2-3 times the calcd. amt. of AcCl it gives practically quant. the chloride, m. 122°, which forms cryst. red double salts with FeCl₃, ZnCl₂, HgCl₂ and SnCl₄. Bromide, m. 143°. B, obtained like A in about 2 g. yield from 4 g. of the chloride and 4 g. Ag, begins to darken in CO₂ at 125°, m. 140-5°. Peroxide, obtained in 79-82% yield, m. 157°. *o*-Phenyl-3-methoxyfluoryl peroxide (D), m. 200°. *p*-Anisylbiphenylenemethyl peroxide, which would be the

product obtained if C had the structure $\text{MeOC}_6\text{H}_4\text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array}$ instead of that given above,

was synthesized and, in agreement with its description by Schlenk and Mair (C. A. 5, 2888), was found to be different from D, which was also synthesized as follows: E with

PhMgBr gave the *carbinol* $\begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{MeOC}_6\text{H}_5 \end{array} \text{CPhOH}$, m. 84°, the *chloride*, m. 119°, with Ag

gives purple solns. of the free *o*-phenyl-3-methoxyfluorol, which with air yield D. Dissociation of *di*-*p*-methoxyhexaphenylethane in various solvents at their f. p. (the first figure gives the % concn. of the soln., the second the % dissociation): ClCH₂CH₂Br 0.99, 36.6; 4.51, 28.2. C₆H₆ 1.47, 27.1; 6.27, 22.1. PhNO₂ 1.32, 30.5; 5.89, 29.4. (CH₃Br)₂ 0.92, 41.7; 3.28, 33.9. *p*-BrC₆H₄Me 1.27, 31.2; 4.98, 30.3. *p*-C₆H₄Cl₂ 1.09, 46.6; 4.05 37.4. C. A. R.

The isomeric esters of benzoylacrylic acid. GRACE P. RICE. *J. Am. Chem. Soc.* 45, 222-38(1923).—The yellow Me and Et esters of BzCH:CHCO₂H (A) (hitherto the only ones known) are transformed on exposure to sunlight into stereoisomeric colorless forms of higher m. p., which are converted back into the yellow forms when exposed to sunlight in solns. contg. a trace of I or Br. That the colorless Me ester is the stereoisomer of the yellow form was shown by its oxidation to BzQH and (CO₂H)₂ and by its formation with MeNO₂ of the same addn. product, BzCH₂CH(CH₂NO₂)/CO₂Me (B), as is obtained from the yellow ester (Kohler and Engelbrecht, C. A. 13, 2028). The yellow Me ester is almost completely decompd. by boiling dil. Na₂CO₃, while the colorless ester gives 60% of the free A, with concd. HCl, however, both esters give a mixt. of A and BzCH₂CH(OH)CO₂H. The free A corresponds in configuration to the yellow ester and is not transformed into an isomer by sunlight, nor has it been possible to obtain, by any of the usual methods, an isomer corresponding to the colorless ester. Both esters give with 1 mol. H₂NCONHNH₂ an addn. product, probably BzCH₂CH(NHNHCONH₂)/CO₂R (C), formed by 1,4-addn. and rearrangement of the resulting product PhC(OH):CHCH(NHNHCONH₂)/CO₂R; this with a 2nd mol. of H₂NCONHNH₂ gives the same compd. PhC(:NHNHCONH₂)CH₂CH(NHNHCONH₂)/CO₂R (D) as is obtained from the colorless ester with 2 mols. H₂NCONHNH₂; concd. HCl converts D back into C. With HNO₃ C gives a NO deriv. BzCH₂CH[N(NO)NHNHCONH₂]/CO₂R (E). The yellow esters with 2 mols. H₂NCONHNH₂ yield products which are probably pyrazolone derivs., CO.NH.N:CPh.CHCl(NHNHCONH₂)/CO₂R (F), formed by elimination of

1 mol. NH₃ and giving C with concd. HCl. The colorless *methyl ester* of A, needles from MeOH, m. 67°, is obtained in 82-90% yield from the lemon-yellow form, m. 34°, exposed several weeks to sunlight in corked test tubes; with MeNO₂ and Na in alc. it gives 70% of B, m. 57°. Numerous attempts were made to prep. an isomer of A: by exposing A to sunlight for months, by using weak acids instead of HCl to liberate the acid from the Na salt obtained by sapon. of the colorless ester, by using AcCl or Ac₂O instead of H₂SO₄ to dehydrate BzCH₂CH(OH)CO₂H, which was prepd. in 77% yield by boiling A 6 hrs. with 30 parts of 1:4 HCl, and by treating BzCH(OH)CH₂CO₂H with Ac₂O or AcCl; the *β*-hydroxybenzoylpropionic acid, needles from Et₂O-petr. ether, m. 116°, was obtained in 58% yield by brominating BzCH₂CH₂CO₂H in CHCl₃ and shaking the resulting *β*-bromobenzoylpropionic acid (m. 126°, yield, quant.) 7 hrs. with 10% Na₂CO₃. *Methyl α-semicarbazinobenzoylpropionate semicarbazone* (D), colorless powder from H₂O, m. 177-8° (rapid gas evolution). *Methyl α-semicarbazinobenzoylpropionate* (C), powder from MeOH, m. 150-0.5°, sol. in HCl and recpdt. by Na₂CO₃; *nitroso derivative* (E), m. 125° (gas evolution), gives the Liebermann reaction. *Methyl semicarbazinomethylphenylpyrazolonecarboxylate* (F) (1.1 g. from 1.3 g. H₂NCONHNH₂·HCl and 1.6 g. NaOAc with the yellow ester of A in MeOH), m. 172° (slow gas evolution). *Ethyl benzoylacrylate*, yellow mobile liquid, *b*₃₅ 184-5°, is obtained in 26 g. yield (not quite pure) by esterifying 34 g. BzCH₂CH₂CO₂H, brominating the resulting ester (35 g. *b*₃₄ 194°) and eliminating HBr in abs. EtOH. Colorless isomer (6.1 g. from 10 g. of the yellow ester exposed 10 weeks to sunlight), m. 54°. *Ethyl α-semicarbazinobenzoylpropion-*

ate semicarbazone, m. 187° (rapid gas evolution). Ethyl α -semicarbazinobenzoylpropionate, powder from MeOH, m. 151–2°, sol. in concd. HCl and reprecipitated by Na_2CO_3 ; nitroso derivative, m. 127° (rapid gas evolution). Ethyl semicarbazinomethylphenylpyrazolone-carboxylate, m. 171° (slow gas evolution). A itself, whether 1 or 2 mols. $\text{H}_2\text{NCONHNH}_2$ are used, whether the reaction is allowed to proceed only 0.5 hr. or overnight and whether the soln. is dil. or concd., always yields the same products: benzoylacrylic acid semicarbazone hydrate, m. 190°, and two isomeric anhydrous semicarbazones, m. 205° and 225°, resp. The hydrate changes on long boiling in H_2O into the compd. m. 205° but in the dry state decomposes before it loses H_2O ; with Br in cold CHCl_3 or AcOH it forms, without elimination of a trace of HBr, the same dibromide, powder, m. 171° (rapid gas evolution) as is obtained from the 205° and 225° compds. in AcOH; this dibromide is extremely sensitive to all solvents and decomposes completely into a yellow liquid on contact with warm solvents.

C. A. R.

Action of bromine water on indene. JOHN READ AND ERIC HURST. *J. Chem. Soc.* 121, 2550–4 (1922).—The interaction between $\text{Br}\cdot\text{H}_2\text{O}(\text{HOBr})$ and indene, either at 2° or 90°, leads to a practically quant. yield of 2-bromo-1-hydroxyhydrindene. At the lower temp. pasty aggregates consisting of the reaction product and unchanged indene form, which prevent the isolation of the reaction product. This difficulty was overcome by the addition of kieselguhr to the mixt. Careful fractionation of the product gave a small amt. of an isomeric substance(?), softening at 85°, and very sol. This method furnishes a convenient process for prep. β -hydrindone, since the bromohydrin, treated with 4% EtOH-KOH, gave a 75% yield of the ketone, m. 58°.

C. J. WEST

Selenium organic compounds. II. Synthesis of diarylthiophenes and diaryl-selenophenes. MARSTON T. BOGERT AND PILAR P. HERRERA. *J. Am. Chem. Soc.* 45, 238–43 (1923); cf. *C. A.* 17, 107.—In view of the ease with which PhCH:NPh condenses to the thiazole $\text{C}_6\text{H}_4\text{N}:\text{CPh:S}$ on fusion with S, it was hoped that a similar

fusion of MePhC:NPh with S would give the p -thiazine $\text{C}_6\text{H}_4\text{N}:\text{CPh.CH}_2\text{S}$ or possibly the thionaphthene $\text{C}_8\text{H}_4\text{C}(\text{NPh})_2\text{S}$, but as a matter of fact there was

obtained a fair yield of 2,4-diphenylthiophene (A) and no PhEt , PhCH:CH_2 or 2,5-diphenylthiophene was detected in the product. It is suggested that the anil is decomposed by H_2S (formed first by side reactions of the S and later as a product of the main reaction) with liberation of the aromatic amine (which distills off) and production of PhCSMe , which in turn condenses as follows: $\text{PhCSMe} \rightleftharpoons \text{PhC(SH):CH}_2 \rightarrow$

$\text{PhC}(\text{CH}_2\text{CH:NPhS}) \rightarrow \text{A} + \text{H}_2\text{S}$. Instead of the anils the tolls may be used equally well and substituted acetophenones can be employed instead of PhCOMe itself. The method can be applied with equal success to the Se compds. Acetophenone-*o*-tolid (323 g. from 380 g. PhCOMe , 475 g. $o\text{-MeC}_6\text{H}_4\text{NH}_2$ and 19 g. $(\text{MeC}_6\text{H}_4\text{NH}_2)_2\cdot\text{ZnCl}_2$ heated 1 hr. at 170–80°, light yellow oil, b_{44} 210–20°, gradually turns brown in the air. *p*-Methylacetophenone-anil (yield, 29.5%), light yellow oil, b_{33} 220–40°. A (10 g. from 60 g. MePhC:NPh and 20 g. S heated 13 hrs. at 220–40°), yellow oil, b_{33} 260–5°, scales from abs. alc., m. 122.5°, practically insol. in H_2O , HCl and alkalis, gives with concd. H_2SO_4 a yellow, with HNO_3 a red color, forms a bluish green ppt. with H_2SO_4 -isatin (indophenine test) and in the Laubenheimer reaction a green solid sol. in Et_2O , alc., AcOH and C_6H_6 with cherry-red color; in the Liebermann reaction the H_2SO_4 is colored green, then dark red; no addn. product is formed with MeI. With *o*- and *p*- $\text{MeC}_6\text{H}_4\text{N}:\text{CMePh}$ instead of the anil, the yields of A were 23.6 and 32.4%, resp. 5-Chloromercuri-2,4-diphenylthiophene (1.5 g. from 1 g. A in 200 cc. of 95% alc.

allowed to stand 6.5 days in the cold with 10 g. of 33% NaOAc and 50 g. of cold satd. HgCl_2 , silky needles from alc., m. 223°. **2,4-Diphenylselenophene (B)** (13 g. from 60 g. $\text{MePhC} : \text{NPh}$ and 48.6 g. Se heated 16 hrs. at 280–95°), reddish oil, b_m 270–80°, scales from abs. alc., m. 112.3°, turned dark red by HNO_3 , sol. in H_2SO_4 with orange color, gives a brown color with isatin- H_2SO_4 and a green color in the Laubheimer reaction, H_2O pptg. green flocks sol. in alc., Et_2O or AcOH with orange, in C_6H_6 with deeper orange color; the Liebermann test gives a green, then a brownish black color. With the *o*- and *p*-tolils the yields are 23 and 29.3%, resp. **5-Chloromercuri derivative** (yield, 89%), fine needles from 95% alc., m. 224°. **2,4-Di-*p*-tolylselenophene**, obtained in 20.5% yield from $\text{Mc}(p\text{-MeC}_6\text{H}_4)\text{C} : \text{NPh}$ and Se heated 11 hrs. at 270°, reddish oil, b_m 260–80°, leaflets from abs. alc., m. 136.3°, sol. in concd. H_2SO_4 with red color, gives with isatin- H_2SO_4 a bright red color and in the Laubheimer reaction a green ppt. sol. in Et_2O with orange-yellow, in alc., AcOH and C_6H_6 with orange, in H_2SO_4 with brown color, diln. of the latter soln. repptg. the green solid; in the Liebermann reaction the H_2SO_4 is colored dark green. In the course of the work, $\text{MePhC}(\text{OMe})_2$, liquid of agreeable floral odor, b_{10} 90°, was prepd. in 20 g. yield from 22 g. $\text{HC}(\text{OMe})_3$, 16.2 g. MeCOPh and 4 drops concd. HCl heated carefully for several hrs. at 40° in a flask with a CaCl_2 guard tube, allowed to stand 16 hrs. and carefully made alk. with alc. NaOMe .

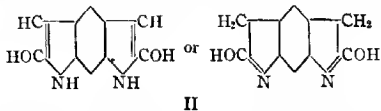
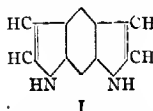
C. A. R.

Thiophenes series. XV. Ring compounds containing mercury and experiments on the preparation of mixed thiophene-mercury compounds. WILHELM STEINKOPF, WILHELM BIELENBERG AND HALVARD AUGSTAD-JENSEN. *Ann.* 430, 41–78 (1922); cf. C. A. 16, 3653.—The reaction between 1 mol. PhMgBr and 0.9 mol. PhHgCl gave a 67% yield of Ph_2Hg . The reaction of a nearly theoretical amt. of HgCl_2 with PhMgBr gave a 55% yield of Ph_2Hg , provided the addn. of the HgCl_2 is not too rapid. The addn. of 1 mol. $\text{C}_6\text{H}_5\text{SHgCl}$ to PhMgBr resulted in the formation of Ph_2Hg , but by the interaction of $\text{C}_6\text{H}_5\text{SMgBr}$ and PhHgCl there resulted a crude product which contained *phenylmercurythienyl*. Upon crystn. this appeared to decomp. into Ph_2Hg and $(\text{C}_6\text{H}_5\text{S})_2\text{Hg}$. Preliminary expts. indicated that PhHgCl or $\text{C}_6\text{H}_5\text{SHgCl}$ may be reduced in $\text{C}_6\text{H}_5\text{N}$ soln. by SnCl_2 , giving Ph_2Hg or $(\text{C}_6\text{H}_5\text{S})_2\text{Hg}$ in 90% yield. Applied to a mixt. of these 2 compds., however, no trace of $\text{PhHgC}_6\text{H}_5\text{S}$ was found. Attempts to prep. unsym. Hg dithienyls by the use of NaI or NaCNS gave only the sym. derivs. The stability of certain Hg compds. was studied by observing the rate of formation of HgS by Na_2S ; the lability of the C-Hg union increased with increasing negativity of the substituent. An app. is described for observing this formation. **2,5,2',5'-Dimercurydithienylene (A)**, $\text{Hg} : (\text{C}_6\text{H}_5\text{S})_2 : \text{Hg}$, results from the action of NaI or NaCNS upon $2,5\text{-C}_6\text{H}_4\text{S}(\text{HgCl})_2$ in $\text{C}_6\text{H}_5\text{N}$, amorphous, insol. in all ordinary solvents, and does not m. 330°. When $2,5\text{-C}_6\text{H}_4\text{S}(\text{HgCl})_2$ is heated alone in $\text{C}_6\text{H}_5\text{N}$ to 100°, **2,2'-dimercuric chloride-5,5'-mercurydithienyl (B)**, $\text{ClHg.Hg} : (\text{C}_6\text{H}_5\text{S})_2 : \text{Hg.HgCl}$, results; this is insol. in all ordinary solvents and does not m. 325°. The limiting concn. for the formation of B appears to be 1 : 30; this gives only a slight turbidity; 1 : 20 gives a ppt. at 100° and 1 : 10 at 82°. B also results by the action of HgCl_2 in $\text{C}_6\text{H}_5\text{N}$ upon a suspension of A in $\text{C}_6\text{H}_5\text{N}$. **3,3'-(or 4')-Diethyl-2,5,2',5'-dimercurydithienylene**, yellowish powder, decomp. 310–15°. This reacts with HgCl_2 as does A, though an excess gives $3\text{-EtC}_6\text{H}_4\text{S}(\text{HgCl})_2$. **3,4,3',4'-Tetramethyl-2,5,2',5'-dimercurydithienylene**, darkens at 310°. **XVI. The constitution of thiophene.** W. STEINKOPF, H. AUGSTAD-JENSEN AND HANS DONAT. *Ibid* 78–112.—This article is devoted to a study of BrCN as a brominating agent. Little is said concerning the structural formula of $\text{C}_4\text{H}_2\text{S}$. With 1.5 mols. BrCN in CS_2 or C_6H_6 , a 45% yield of pure $\text{C}_4\text{H}_2\text{Br}_2\text{S}$ is obtained with some $\text{C}_4\text{H}_2\text{Br}_3\text{S}$. $\text{C}_4\text{H}_2\text{Br}_3\text{S}$ and 1.5 mols. BrCN , heated 10 hrs. at 90–100°, gave 34% $\text{C}_4\text{H}_2\text{Br}_3\text{S}$. With ICN a trace of $\text{C}_4\text{H}_2\text{IS}$ is formed. Ten g. $2\text{-MeC}_6\text{H}_4\text{S}$ and 15 g. BrCN gave 4.4 g. $\text{C}_6\text{H}_2\text{Br}_3\text{S}$, b. 173–7°.

$\text{AcCH}_2\text{CO}_2\text{Et}$ and BrCN at 100° gave a mixt. of the γ - and α -Br esters. BzMe and BrCN at 110 – 15° gave 31% ω -Br deriv. 2-Acethiothione and BrCN gave a considerable amt. of the ω -Br deriv., identified by transformation into $\text{C}_6\text{H}_5\text{SCOCCH}_2\text{NHPH}$. Indene and BrCN gave indene hydroxybromide. 5-Ethyl-2-propiothienone, b_{13} 137– 8° . Semicarbazone, m. 195 – 6° . 5-Propyl-2-propiothienone, b_{13} 137.5– 8.5° . Semicarbazone, prisms, m. 174 – 5° . 5-Isoamyl-2-acethiothione, b_{13} 149– 51° . Semicarbazone, leaflets, m. 212° . 2-Ethyl-5-propylthiophene, by the reduction of the ketone in HCl with Zn-Hg , b. 196 – 7° . 2,5-Dipropylthiophene, b. 213 – 4° . 2-Ethyl-5-isoamylthiophene, b_{13} 103.5– 6.5° . 3-Bromo-2,5-dipropylthiophene, b_{16} 130– 2.5° . Bromoethylisoamylthiophene b_{14} 122– 7° .

C. J. WERT

Synthesis of m - α -benzispipyrrole derivatives. WM. DAVIES AND E. H. C. HICKOX. *J. Chem. Soc.* 121, 2640–55(1922).—The synthesis of new cyclic systems which should, from analogy with simpler naturally occurring systems, be found in nature has been undertaken. m - α -Benzispipyrrole (I), from its structural similarity to indole, should be the product of vital syntheses. The 1st line of attack was the condensation of 2,4,6,3,5-Me₅C₆H(NO₂)₂ with 2 mols. $(\text{CO}_2\text{Et})_2$ in the presence of EtONa (4 atoms Na) at 40° , which gave dinitro- m -xylylpyruvic acid, deep yellow plates, m. 174 – 7° (decompn.). No modification of the conditions gave a condensation product in which both Me groups had reacted. The use of higher temp. resulted in the decompn. of the monopyruvic ester 1st formed, and there probably resulted 2,4-dinitro-5-methylphenylpyruvic acid, microcrystals, sinters 250° , does not m. 300° , gives a blood-red color in NaOH and suddenly deflagrates when cautiously heated in a flame. The condensation of 2,6,3,5-Cl₄C₆H(NO₂)₂ with $\text{AcCHNaCO}_2\text{Et}$ in EtOH gives ethyl 5-chloro-2,4-dinitro-6-methylphenylacetate, stout yellow crystals, m. 92 – 3° , sol. in NaOH with a red color. It is not easy to replace the 2nd Cl group in this compd. and so this method was also abandoned. The condensation of 1,3,4,6-Cl₄C₆H(NO₂)₂ with $\text{AcCHNaCO}_2\text{Et}$ in C_6H_6 by boiling for 12 hrs. gave ethyl 4,6-dinitrophenylene-1,3-diacetate (A), bright yellow, m. 108.5° . At the same time there is formed 1,3,4,6-(EtO_2CCH_2)₂C₆H(NO₂)₂ (Borsch and Babr, *C. A.* 7, 664). The production of this ester is favored by the prolongation of the time of condensation and by the presence of EtOH . There is also obtained a small amt. of a substance C₁₄H₁₀O₆, m. 168 – 9° , identical with that obtained by Collie and Chrystall (*C. A.* 2, 815) by heating $\text{AcCH}_2\text{CO}_2\text{Et}$ with its Na deriv. in EtOH (see also Perkin and Thorpe, *J. Chem. Soc.* 71, 1194). Hydrolysis of A gave the free acid, the lead salt of which is very slightly sol. in cold H_2O . The NH₄ salt, treated with FeSO_4 in H_2O , gives 2,6-dihydroxy- m - α -benzispipyrrole (II), silky needles, partly m. and decomp. 300 – 50° . It sublimates at 30 mm. with some decompn. It is a very weak base. The aq. soln. gives no color with FeCl_3 and reduces $\text{NH}_4\text{OH-AgNO}_3$ and KMnO_4 in the cold. Sodium salt, light brown prisms, contg. H_2O of crystn. The di-Na salt is very sol. in cold H_2O . II reacts with BzH contg. a trace of $\text{C}_6\text{H}_5\text{N}$ to give 2,6-diketo-3,5-dibenzylidene-2,3,5,6-tetrahydro- m - α -benzispipyrrole, deep orange rhombohedrons, m. 315° (decompn.). The cold concd. H_2SO_4 soln. is deep orange without fluorescence, and H_2O ppts. an amor-



phous yellow substance. Attempts to prep. a pure oximino deriv. failed. A crude red 2,3,5,6-tetraketo deriv. was also prepd.; this gives an intense deep green color when warmed with thiophene.

C. J. WERT

Orientation of the 1,4- and 1,5-dimethylglyoxalines. Mode of fission of 5-amino-glyoxalines. F. L. PYMAN. *J. Chem. Soc.* 121, 2616–26(1922); cf. *C. A.* 4, 79.—No

conclusive evidence has been produced in support of the formulas of the 2 dimethylglyoxalines, which is important because the orientation of the higher boiling base forms a step in the detn. of the constitution of pilocarpine and because a study of suitable derivs. will bring to light the properties of substituents in both the 4- and 5-positions of the glyoxaline nucleus. The method adopted was an examn. of the reduction products of the NO_2 derivs. of the 2 isomerides (cf. Fargber, C. A. 14, 3219). 4-Methylglyoxaline is conveniently methylated by the action of MeI in C_6H_6 . 1,4-Dimethylglyoxaline nitrate (A) forms long needles, m. $103-4^\circ$, and the 1,5-isomer (B) large prisms, m. $128-9^\circ$. The NO_2 derivs. may be prepd. by nitration of the Me_2 derivs. or by methylation of 5-nitro-4-methylglyoxalinc. A gave the 5-nitro derivative (C) (obtained in 67.5% yield by the 2nd method), long prismatic needles, m. $57-8^\circ$, b₁₆ 155° ; picrate, stout yellow needles, m. 176° , sol. in about 1000 parts cold H_2O . The 4- NO_2 deriv. (D) (obtained in 0.29% yield by the 2nd method) is identical with Windaus's "nitro- α -N-dimethylimidazole" (C. A. 3, 1268); the picrate forms pale yellow, large prisms, m. $66-9^\circ$; it dissolves in about 50 parts cold H_2O . The reduction of C with SnCl_2 and HCl gave, besides dl-alanine, NH_3 and MeNH_2 , dl-alanine-N-methylamidine (E), $\text{H}_2\text{NC}(\text{NMe})\text{CHMeNH}_2$, isolated as the picrate, yellow, elongated prisms, m. 200° (decompn.), sol. in 625 parts cold H_2O ; dihydrochloride, large prisms, m. 242° ; the constitution was established by hydrolysis, yielding MeNH_2 and dl-alanine; and 5-amino-1,4-dimethylglyoxaline (F), also isolated as the picrate, long, stout, orange needles, m. 209° (decompn.); hydrochloride, grayish white prismatic needles, m. 253. The free base(?) was obtained as diamond-shaped plates, m. 160° . The reduction of D gave dl-N-methylalanine, NH_3 , and the 4-amino derivative (G), isolated as the picrate, brownish yellow plates, m. 220° (decompn.); hydrochloride, grayish white spikes, m. 225° . The corresponding base(?) was obtained as small prisms, m. 85° . The isolation of E is important in showing that in this case at least the mechanism of the degradation of the aminoglyoxaline to the NH_2 acid is due to the elimination of the C atom in the 2-position by hydrolysis. The NH_2 group in F and G has an aromatic character, since both amines after diazotization gave solns. which coupled with $\beta\text{-C}_{10}\text{H}_7\text{ONa}$ but gave no marked color with NaOH . Both amines appear to give benzylidene derivs. and reduce hot $\text{NH}_4\text{OH}\cdot\text{AgNO}_3$. Neither gives a color with FeCl_3 but with alk. $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$ F gives an immediate brownish yellow color while G gradually develops a lemon-yellow color.

C. J. WEST

Bromo derivatives of 2-methylglyoxaline. LOUIS LIGHT AND F. L. PYMAN. J. Chem. Soc. 121, 2326-30 (1922).—The product considered by Radziszewski as tribromo-2-methylglyoxaline (Ber. 15, 2707) is shown to be the 4,5-dibromo hydrobromide; this seps. as irregular prismatic needles in the reaction of Br upon 2-methylglyoxaline, chars about 280° ; hydrolysis yields 4,5-dibromo-2-methylglyoxaline, long silky needles, darkens 236° , m. $239-40^\circ$; it is sol. in about 350 parts boiling H_2O , almost insol. in cold. Hydrochloride, chars about 255° . On reduction of the base with Na_2SO_3 , the 4-bromo derivative results, short, stout rods from H_2O or elongated plates from CHCl_3 , m. $162-3^\circ$, sol. in about 10 parts boiling H_2O , giving a slightly alk. soln. It gives a cherry-red soln. with $p\text{-HO}_3\text{SC}_6\text{H}_4\text{N}_2\text{ONa}$ in Na_2CO_3 . Hydrochloride, quadrilateral plates with H_2O , m. $187-8^\circ$. Nitrate, silky needles, decomp. 132° . Picrate, yellow prismatic needles, m. $161-3^\circ$. Nitration gives the 4-bromo-5-nitro derivative, microneedles, m. 268° (decompn.). On exposure to bright sunlight, it becomes pale green in color. The 5-sulfonic acid crystals, in elongated prisms, sinters 255° , m. 266° (decompn.). The H_2O of crystn. is not lost at 120° . It is sol. in about 14 parts boiling H_2O and in more than 100 parts cold H_2O . Hydrolysis with 36% H_2SO_4 gave the pure 4-Br deriv.

C. J. WEST

Hydroxycodine series. EDMUND SPEYER, S. SELIG AND MARTIN HELL. Ann. 430, 1-40 (1922); cf. Freund and Speyer, C. A. 11, 3263.—In repeating the earlier methods of prepn. of 7-hydroxycodine (A) it was found that the yield was poor and that smears

products resulted from which no cryst. material could be isolated. The yield is considerably increased by carrying out the reduction of hydroxycodeinone (B) with Zn dust (treated with CuSO_4) in 85% HCO_2H , the reaction requiring about 15 min. at room temp., and pptg. the product as the ZnBr_2 double salt. When this is decompd. with 25% NH_4OH and the solid base extd. with CHCl_3 , a part, *hydroxythebainol* (C), $\text{C}_{18}\text{H}_{21}\text{O}_4\text{N}$, is insol. and seps. from $\text{CHCl}_3\text{-EtOH}$ in prisms, m. 234° . It also results by the electrolytic reduction of B in 25% H_2SO_4 , with 5 amp. and Pb electrodes. *Hydroiodide*, yellowish white prisms with H_2O , m. 247° . *Hydrobromide*, small prisms, m. $252\text{--}3^\circ$, $\alpha_D -157.7^\circ$ (c 1.5940 in H_2O). *Picrate*, golden yellow needles, m. $204\text{--}6^\circ$. *Monobenzoate*, needles, decomp. 257° . *Monobromide*, by adding Br-AcOH to C in AcOH until no more perbromide seps. and then heating with H_2SO_4 until soln. results, needles, m. $230\text{--}1^\circ$; H and Pt in AcOH regenerate C. Warmed with 30% H_2O_2 until soln. results, C yields a *N-oxide*, prisms, decomp. 237° . In the formation of C there are also formed varying amts. of C *formate*, insol. in CHCl_3 , needles, m. 227° . *Hydroiodide*, prisms, decomp. above 305° . When an alk. soln. of C in 10% NaOH is shaken with Me_2SO_4 and then treated with KI, the *methyl ether methiodide* (D) results, small rhomboids, decomp. 233° . The addn. of concd. KOH to aq. D gives *des-N-methylhydroxythebainol methyl ether*, small needles, m. $195\text{--}7^\circ$. Its insoly. in NaOH indicates the presence of the MeO group. *Hydroiodide*, needles contg. 3 H_2O , m. 255° . MeI gives the *methiodide* (E), small prisms, decomp. $239\text{--}40^\circ$, $\alpha_D 141.8^\circ$ (c 1.2792 in H_2O). E, freed of I with Ag_2O and then heated on the H_2O bath with KOH until the Me_2N is completely split off, gave a *N-free compound*, $\text{C}_{18}\text{H}_{21}\text{O}_4$, compact prisms, m. $188\text{--}9^\circ$, $\alpha_D -29.01^\circ$ (c 1.814 in CHCl_3); this is insol. in NaOH . *Acetylhydroxycodine methiodide*, small prisms, decomp. 256° . *Hydroxythebainone* (F), compact columns, decomp. $104\text{--}6^\circ$. *Dibromide*, small rods, decomp. 258° . *Methiodide*, prisms, m. 245° . *Monoacetate*, prisms, m. 197° . *Acetate oxime*, prisms, m. $216\text{--}8^\circ$. *Acetate methiodide*, columns, m. $212\text{--}3^\circ$. Attempts to reduce the oxime of F to an amine (in alk. soln.) gave only dihydrohydroxythebainone, NH_2 being split off, while reduction in acid soln. led to dihydrohydroxycodeinone. In the same way MeC(=NOH)CH:CHPh gave $\text{MeCOCH}_2\text{CH}_2\text{Ph}$, and $(\text{PhCH:CH})_2\text{C:NOH}$ gave $(\text{PhCH}_2\text{CH}_2)_2\text{CO}$ and NH_3 .

C. J. WEST

Absorption colors of the second order (PICCARD) 25. Some new hypnotics of the harbituric acid series (SHONLE, MOMENT) 11H.

LIHSENGANG, R. E.: *Wissenschaftliche Forschungsberichte*. Bd. III. *Organische Chemie*. Dresden and Leipzig: Th. Steinkopff. 182 pp. M60. Reviewed in *Kolloid Z.* 31, 54(1922).

PERRIN, W. H. and KIPPING, F. S.: *Organic Chemistry*. Revised Ed. London: W. & R. Chambers. 681 pp. 8s 6d. Reviewed in *Chem. Age* (London) 7, 673.

Acetaldehyde from acetylene. L. F. M. TREVOUX. U. S. 1,436,550, Nov. 21. C_2H_2 is hydrated in the presence of a catalyzer consisting of a mixt. formed of Hg , H_2SO_4 and an oxidizing agent which maintains the catalyzing action of the Hg indefinitely. Cf. C. A. 16, 3665.

Aldol from acetaldehyde. N. GRÜNSTEIN. U. S. 1,437,139, Nov. 28. AcH contg. HOAc is freed from the latter and then condensed to form aldol by use of aq. NaOH . If the reaction becomes too violent, acid is added to check it.

Separating different chloroacetones from each other. H. E. BUC. U. S. 1,436,940, Nov. 28. A mixt. of di-, tri-, tetra- and penta-chloroacetones is extd. with H_2O to obtain an aq. soln. principally contg. tri- and tetrachloroacetones, the aq. soln. is sepd. and the chloroacetones are "salted out" from it and fractionated. The extn. residue is extd.

with an aq. soln. of NaHSO_4 to dissolve the dichloroacetone, which is later recovered from the sepd. decomposed soln.

Isopropyl chloride from isopropyl alcohol. H. E. BUC. U. S. 1,436,377, Nov. 21. HCl is introduced into isopropyl alc. and isopropyl chloride is recovered by distn. at atm. pressure.

Chlorination of isopropyl alcohol. H. E. BUC. U. S. 1,436,378, Nov. 21. Chlorinated acetones are prepd. by subjecting isopropyl alc. to the action of Cl at a temp. of $35-70^\circ$.

Alkyl ethers of vinyl alcohols. H. PLAUSON. U. S. 1,436,288, Nov. 21. Cold anhyd. H_2SO_4 96 is gradually satd. with C_2H_5 26-28 parts at a pressure of 2-5 atm. and a temp. of 0 to -15° . Vinylsulfuric acid is thus obtained in almost quant. yield. The reaction is facilitated by the presence of HgSO_4 as a catalyst. The vinylsulfuric acid is converted into the corresponding ether by reaction with EtOH or with normal or isopropyl alc. by warming under reduced pressure. Etherification may also be effected by introducing the C_2H_5 into H_2SO_4 to which the alc. has previously been added.

Stabilizing acrolein. C. MOUREU. U. S. 1,436,047, Nov. 21. Transformation of acrolein into diacryl is prevented by the addn. of PhOH , pyrogallol, pyrocatechol, hydroquinol, gallic acid or tannin 0.1-1.0%.

Coumarin. C. C. LOOMIS. U. S. 1,437,344, Nov. 28. The reaction mixt. obtained by heating together salicylaldehyde, NaOAc and Ac_2O is mixed with milk of lime and heated and the filtrate obtained from the heated mixt. is treated with HCl . Coumarin is then sepd. on liberation from its Ca salt and solidification.

Urea from cyanamide. J. H. LINDHOLM. U. S. 1,436,180, Nov. 21. A soln. of cyanamide is reacted upon by H_2SO_4 or other inorg. acid and the heat liberated is utilized for partial evapn. of the soln. or for heating liquid in a boiler.

11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

The nature of diastatic enzymes. W. BIEDERMANN. *Münch med. Wochschr.* 68, 692-3(1921); cf. *C. A.* 16, 3908.—Human saliva contains a protein of albumose character which possesses diastatic activity. The reactions characteristic of this substance can be shown in various solns. having diastatic activity. S. AMBERG

The diastatic action of albumoses and amino acids. W. BIEDERMANN. *Arch. néerland. physiol.* 7, 151-6(1922).—*Proteins, albumoses, polypeptides and amino acids are found to have a distinct diastatic action on starch (amylose) at 45° .* B. first succeeded in observing this diastatic action with "atmidal-albumin" or "at midal-albumose," a peculiar protein, first prepd. by Neumeister (*Z. Biol.* 26 (1890)) by heating 3-4 g. coagulated pure fibrin with 20 cc. water in closed glass-tubes to $160-170^\circ$ for 1 or 2 hrs. A colloidal soln. of "atmidal-albumoses" exhibits all the chem. reactions peculiar to the albumoses contained in the saliva, viz.: it is pptd. by HNO_3 and other acids; this ppt. is dissolved by heating and reappears, on cooling down again; also the huiuret reaction has very much the same appearance with both albumoses. As the diastatic action of the albumoses in the saliva was known it seemed likely that the atmidal albumoses too might act similarly, considering the similarity of chem. reactions, although their origin is an entirely different one. As a matter of fact this assumption proved to be justified; the diastatic action was found to be very great,—5 cc. 1% starch-soln.

being decompd. entirely within 1 or 2 hrs. by 5 cc. of the "atmidal-soln.," prepd. as described above. The analogy between this action and the one of the albumoses of saliva is still more striking considering that in both cases the presence of the same ions (Na^+ and Cl^-) and of O is necessary. It is ascertained by control expts. that this diastatic action is *only* due to the albumoses, not, *e. g.*, to bacteria accidentally present. Furthermore, various other albumoses, *e. g.*, the ordinary ones occurring in digestion, were investigated; they also have an amylolytic action, although to a much smaller degree. Also polypeptides and pure crystd. amino acids (glycine, leucine, alanine) were found to be active. These observations explain the statements, found in the older literature, about an increase of amylolysis, produced by amino acids (cf. Ellfront, *Compt. rend. soc. biol.* 57, 234(1904)), and TERROINE AND WEIL (*J. Physiol. path. gen.* 14, 437(1912) cf. *C. A.* 7, 1535).

R. BEUTNER

The physical chemistry of hemoglobin in blood. W. E. L. BROWN AND A. V. HILL. *Arch. néerland. physiol.* 7, 174-8(1922).—The conception of a reversible chem. combination of hemoglobin with O, together with the full application of thermodynamical reasoning to it, has not been generally accepted, and it has been suggested that the combination is really of the rather indefinite phys. kind referred to generally as "adsorption." Against this it may be urged that: (1) the relation of Fe to O, reversibly bound, as oxyhemoglobin, is exactly as one atom to two; (2) the different compds. (reduced, oxygenated and carbonylhemoglobin) have highly sp. absorption bands; (3) they have sometimes different crystallographic characters. The authors find still another proof by applying van't Hoff's isochore. The change of the dissociation-const. of the reaction: $\text{Hb}_n + n\text{O}_2 \rightleftharpoons (\text{HbO}_2)_n$ agrees with the value calcd. from the heat developed by this reaction.

R. BEUTNER

Decarboxylations. K. SPIRO. *Arch. néerland. physiol.* 7, 227-33(1922).—Histamine is not an essential constituent of *secale cornutum* nor of *hypophysis preps.* The action of secale on the uterus is due to ergotamine and ergotamine. Also, the hypothesis that histamine is an endocrine hormone, generated from histidine by decarboxylation, does not seem to be justified. Decarboxylations of proteins or amino acids do not seem to take place in the organism. Only substances contg. no N, like sugars, aliphatic acids, etc., are decarboxylated in metabolism. Referring to the work of Neuberg on decarboxylations in fermentations S. develops extensive hypotheses concerning the chem. transformations in question. The formation of glucose from fumaric acid as observed by M. Cremer in exptl. diabetes is assumed to occur according to the following equations: $\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH} + \text{O} = \text{COOH} \cdot \text{CH} \cdot \text{CH} \cdot \text{COOH} + \text{H}_2\text{O}$; $\text{COOH} \cdot \text{CH} \cdot \text{CH} \cdot \text{COOH} + \text{H}_2\text{O} = \text{CH}_3 \cdot \text{CHOH} \cdot \text{COOH} + \text{CO}_2$; and $2\text{CH}_3 \cdot \text{CH} \cdot \text{COOH} = \text{C}_4\text{H}_{12}\text{O}_4$.

R. BEUTNER

The problem of hydrogen activation by the cells. TORSTEN THUNBERG. *Arch. néerland. physiol.* 7, 240-4(1922).—Lipschitz and Gottschalk (*C. A.* 16, 2525) have found that the colorless *m*-dinitrobenzene is reduced to *m*-nitrophenylhydroxylamine, which has a distinct yellow color, under the action of an ext. of frog muscle and certain org. acids, like succinic acid, fumaric acid and others. L. and G. could *not* state, however, a difference between the actions of the *d*- and *l*-tartaric acids in this reaction. This would be in contradiction with previous results obtained by the author studying a similar reduction with methylene blue instead of *m*-dinitrobenzene. Repeating the expts. of L. and G. with his own app. (evacuated tubes) the author finds also that a striking difference between *d*- and *l*-tartaric acid can be observed in the reduction of *m*-dinitrobenzene. While the *l*-acid considerably accelerates the reduction; such is not the case with the *d*-acid. Also, maleic acid proves to have a slight catalytic action in contradiction with the statements of L. and G. Further expts. are described which prove that methylene blue and *m*-dinitrobenzene accelerate the oxidation of thioglycolic acid and of grape sugar.

R. BEUTNER

Conduction of the electric current in the human body. W. EINTHOVEN AND J. BJRTEL. *Arch. néerland. physiol.* 7, 407-14(1922).—The intensity of the elec. current passing through the human body depends on the resistance, the polarization, and the electrostatic capacity. These 3 magnitudes are detd. with alternating as well as with continuous current. The resistance of the body is composed of the resistance of the inner parts and of the relatively high resistance of the epidermis; the latter makes the skin an imperfect condenser. The resistance of the skin, as well as the polarization, decreases if a strong current passes; both effects are due to an immigration of ions into the epidermis. With an a. c. circulating in the body, the apparent resistance is the smaller the higher the frequency. If a self-induction is contained in the circuit the apparent resistance may even become negative, which is due to the capacity of the skin. This capacity was found to equal 6.3×10^{-7} for the skin of the fingers in one case; in another case 7.7×10^{-7} microfarads per sq. cm. was found. R. BEUTNER

Physical chemistry of foodstuffs. VI. The sensation of sour taste. T. PAUL. *Z. Elektrochem.* 28, 435-46(1922); cf. *C. A.* 16, 973.—Methods previously employed for investigating the sourness of acids, among them the swelling-value method, are affected by serious errors. The method recently employed by P. in studying the sweet taste of sugars has been found applicable to the detn. of the sour taste of acids. The stimulation of sour taste is due to the H ion. In addn. to the concn. of the actual H ions, that of the potential ions also appears to play a rôle. Acids of approx. the same dissoc. const., such as acetylactic acid and tartaric acid, as well as isohydric solns. of acids, have very different sour tastes, owing to the participation of both the anion of the acid and the undissociated mols. in stimulating this taste. Sour taste cannot be explained by the theory of elec. dissoc. alone. It appears that sour taste depends on the vapor pressure of the acid. The introduction of new definitions and units (analogous to those used for sweet taste, cf. *C. A.* 15, 3881), such as degree of taste, acidity (sourness), sp. and mol. acidity (sourness), sour-degree ratio, etc., simplifies the phenomena of sour taste. By the numerical detn. of sp. acidity, it is possible to calc. the concns. of "isosour" solns. The unit of acidity (sourness) is especially adapted in practice for the prepn. of solns. of acids which are to have a definite acidity (sourness). The following acids are arranged in the order of increasing sp. or mol. acidity (sourness): H_2CO_3 , cream of tartar, HOAc, lactic acid, acetylactic acid, HCl and tartaric acid. This order differs markedly from the arrangement according to the dissoc. consts. of the acids. The mol. acidity (sourness) of acids is not a const. quantity, but slowly increases with decreasing acid concn. Sour taste and sweet taste are analogous, in so far as the sp. sourness of acids and the degree of sweetness of certain artificial sweet substances, such as saccharin and dulcin, change considerably with concn. Certain analogies between sweet taste and sour taste lead to the supposition that the 4 qualities of taste, sweet, sour, salt and bitter, have similar relations. H. JERMAIN CREIGHTON

Artificially produced cell division and karyokinetic figures. R. BEUTNER AND M. BUSSE. *Z. ges. expil. Med.* 28, 90-5(1922).—The salts of higher mol. wt. stimulate ester formation more readily than salts of lower mol. wt. Na, NH_4 and the chlorides are inert while K, Rb and Cs salts are very active as are also certain neutral org. substances such as glucose, glycerol and urea. E. B. FINK

Biological studies of adsorption from solutions of different salts. F. FICHLER AND A. WÖBER. *Biochem. Z.* 132, 420-38(1922).—Studies of the adsorption of 0.1% $CaSO_4$ by corn-blight spores showed that the protoplasm of this organism is more acid than alk. Other studies showed that the adsorbability depends on whether free or complex ions of the effective metal are present; whether the complex ion is positive or negative; and on the degree of ionization of the salt. The greater the ionization of the salt or positive metal complex, the greater the adsorption and the greater the biol.

effect. Adsorbability is also dependent on the size of the adsorbing complex.

F. S. HAMMETT

Melanins from adrenaline. P. SACCARNI. *Biochem. Z.* 132, 439-42(1922).—Adrenaline-HCl soln. was treated with Cl water and allowed to stand. A black ppt. possessing the characteristics of the pyrroles was obtained.

F. S. HAMMETT

The isoelectric point of globin. S. OSATO. *Biochem. Z.* 132, 485-7(1922).—The pptn. optimum of globin prepd. from sheep corpuscles in various H-ion concns. was studied. The H-ion concn. was detd. colorimetrically. The value lies between p_H 7.8 and 8.3 and is given as 8.1 ± 0.1 . The significance of this alk. isoelec. point in relation to existing conceptions of the colloid state and chem. constitution is briefly noted.

F. S. HAMMETT

The hydrolysis of proteins with strong sulfuric acid. E. SALKOWSKI. *Biochem. Z.* 133, 1-20(1922).—Horn substance, proteins and gelatin are totally hydrolyzed without the formation of humin substances in 2 or 3 hrs. on heating with H_2SO_4 2 vols. and H_2O 3 vols. in the proportion of 1 part by wt. of protein to 3 vols. of H_2SO_4 . The hydrolysate from the horn substance contains practically the entire S content of the original material, some 1.9% by wt. of the NH_2 , but almost none of the aromatic groups. The latter finding holds true for protein and casein. The hydrolysates contain substances which reduce Fehling soln. representing some 12 to 13% of sugar. The reducing substances are largely precipitable by phosphotungstic acid. All hydrolysates contain pyruvic acid and traces of aliphatic aldehydes and furfural. F. S. H.

Isolation of the thyroid hormone. B. ROMEIS. *Biochem. Z.* 133, 97-111(1922); cf. *C. A.* 17, 112.—Normal thyroid glands of freshly slaughtered sheep were minced, mixed with 10 times the amt. of hot satd. $Ba(OH)_2$ soln. and cooked under a reflux condenser until no biuret reaction was given (12 to 14 days). The cooled ext. was treated in 3 ways. The 1st method consisted in neutralizing with H_2SO_4 and filtering off the yellowish $BaSO_4$ ppt. The filtrate and washings were concd. on the water bath to a protein-free sirup. This material induced accelerated development of frog tadpoles, but more slowly than that caused by iodothylin. The 2nd method consisted of pptg. the Ba from the hydrolyzed ext. by CO_2 and making the reaction alk. with Na_2CO_3 . The $BaCO_3$ was removed by filtration and washed. The combined filtrates were concd. and neutralized with AcOH. The sirup was very active in promoting tadpole development, thus indicating that in neutralization with H_2SO_4 the greater part of the active principle is carried down with the $BaSO_4$. The 3rd method consisted of neutralizing the $Ba(OH)_2$ with HCl. $BaCl_2$ remained in soln. and the active part was pptd. out and filtered off after standing for several hrs. Further purification was obtained by repeated soln. in dil. NaOH and reprecipn. with AcOH. Very small amts. of the dry ppt. sufficed markedly to accelerate tadpole development. Further purification was obtained by repeated extn. with 90% alc. slightly acidified with AcOH and evapn. of the alc. from the filtrate. The final product was washed with water-free Et_2O and petr.-ether. The product contains much I and appeared to be like thyroxin.

F. S. HAMMETT

The behavior of uric acid in protein solutions. L. PINCUSSEN. *Klin. Wochschr.* 1, 1462-3(1922).—If a $LiCO_3$ soln. of uric acid is mixed with a soln. of egg white or serum, and the liquid then analyzed for uric acid by one of the standard methods (such as that of Folin-Wu) only a small fraction of the uric acid that was added can be accounted for. The uric acid is apparently absorbed by the coagulum. If such a soln. is aseptically digested with trypsin after the addition of a suitable phosphate buffer, the quantity of the uric acid that can be detd. steadily increases and finally reaches 100%. Digestion with pepsin in acid medium gives similar results. When normal serum is digested with trypsin, the uric acid content, as measured by the Folin-Wu method, usually increases, although this is not invariably true. MILTON HANKE

Comparative studies on respiration. XXIII. The effect of adrenaline on the production of carbon dioxide by animals and by plants. DOROTHY M. HUTCHINSON. *Am. J. Physiol.* **62**, 192-6(1922).—CO₂ production was measured by the method of Osterhout (*C. A.* **13**, 213). Adrenaline has similar effects on the respiration of frogs muscle and of radish seedlings. Stronger solns. (0.002 to 0.003%) cause a depression followed by a return to normal, probably as the adrenaline is oxidized. Weaker solns. (0.002 to 0.005) produce a rhythmic effect; the rate of CO₂ production falls, rises, then falls and rises again.

J. F. LYMAN

The permeability to dyestuffs of the placenta of the albino rat and the white mouse. Y. ZHIMIDZU. *Am. J. Physiol.* **62**, 202-24(1922).—Whether dyes penetrate the placenta depends on the size of the particles of the dyes in the blood, the placenta acting as an ultra-filter. In view of the size of the colloidal particles that can pass the placenta it is inferred that proteins must be decompd. into their components in order to pass from mother to fetus.

J. F. LYMAN

The influence of changes of concentration of the hydrogen-hydroxyl ions on the life of the tissue cells of vertebrates. I. The influence of temporary changes of reaction of the medium. A. A. KRONTOVSKI AND V. V. RADZIMOVSKA. *J. Physiol.* **56**, 275-82(1922).—Small pieces of rabbits spleen were immersed in various buffer solns. of different p_H values for 30 mins. and then transferred to a culture medium of rabbits plasma serum and incubated at 38°. The max. p_H in lactic acid mixtures which left the cells still alive and capable of growth was 4.04; with AcOH mixtures it was 5.33. The min. p_H compatible with life was 10.28. The different spleen cells are not affected to the same degree by changes in p_H . The fibroblasts withstand an increase in acidity which completely inhibits the vital activity of the wandering spleen cells—lymphocytes, reticular polyblasts, etc.

J. F. LYMAN

The influence of oxygen and carbon dioxide on the coagulability of blood. J. MELLANBY AND H. M. G. LESTER. *Proc. Physiol. Soc., J. Physiol.* **56**, xxxiv(1922).—The gases of the blood influence its coagulability to a small degree only. The particular change which diminishes the coagulability of peptone blood also diminishes its capacity to carry CO₂.

J. F. LYMAN

The influence of bile salts on the rate of diffusion between two liquid interfaces. J. COLLINGWOOD AND V. G. WALSH. *Proc. Physiol. Soc., J. Physiol.* **56**, xxxv(1922).—The amt. of interchange between acid and alk. solns. in contact with each other does not appear to be affected by the presence of bile salts, hence surface tension plays no part in the process.

J. F. LYMAN

The alkalinity of the ultrafiltrate of the blood plasma. T. H. MILROY. *Proc. Physiol. Soc., J. Physiol.* **56**, xxxvi(1922).—At a reaction corresponding to p_H 4.2 (neutral point of bicarbonate) substances other than bicarbonates in ultrafiltrates of horse plasma act as bases. There are slight but distinct differences in the alk. of ultrafiltrates of arterial and venous blood plasma, the venous plasma ultrafiltrate having the higher alk. There is a still greater difference in the alk. of ultrafiltrates from evacuated whole blood and blood charged with CO₂, the colloidal alk. reserve of the blood cells thus forming a more important source of disposable alk. than that associated with plasma colloids.

J. F. LYMAN

The absence of relation between the respiratory movement and the reaction of the blood. MELLANBY. *Proc. Physiol. Soc., J. Physiol.* **56**, xxxviii(1922).—In the anesthetized animal CO₂ and lack of O₂ (breathing N₂ or CO) produce marked increases in respiratory movement with very little change in the reaction of the blood; while the intravenous injections of lactic acid and Na₂CO₃ produce great change in the reaction of the blood with small effects on the amplitude of the respiratory movement.

J. F. LYMAN

The lipoids. H. ISCOVESCO. *Presse med.* 30, 653-5(1922).—A review. I. proposes the term *adipoids* to include true fats, fatty acids, lipoids, waxes, cholesterides, protagons and cerebrosides. The relation of lipoids to immunological processes, nutrition, especially to vitamins, blood degeneration and to endocrine insufficiency are discussed, and lipid therapy in the 2 latter conditions is suggested. W. A. P.

Mechanism of the functioning of adipose cells. A. POLICARD. *Compt. rend.* 175, 534-6(1922); cf. *C. A.* 16, 3951.—The mitochondria apparently play no part in the functioning of adult adipose cells. The histologic changes which are seen in adipose cells are explained as being analogous to the interconversion of colloidal types in mixts. of oil and water wherein there may be a little oil, representing an internal phase, dispersed through much water, representing an external phase. As the proportion of oil increases a point is reached at which the water becomes the internal phase and the oil the external phase. Cf. following abstract. L. W. RIGGS

Functioning of adipose tissue; study of the nuchal gland of rodents. A. POLICARD. *Compt. rend.* 175, 726-8(1922); cf. *C. A.* 16, 3951 and preceding abstract.—This gland contains 2 types of adipose lobules, one brownish and opaque, the other white and translucent. The difference of colloidal constitution of the fat in these 2 varieties of lobules is readily shown by spot testing with tissue paper. When in a mixt. of water-oil the internal phase is oil and the external phase is water: the mixt. wets tissue paper without leaving a grease spot. The stain formed will dry and quickly disappear. When in a mixt. of water-oil, water forms the internal phase; the mixt. will not wet paper but will form a persistent grease spot. The brownish lobules of the adipose tissue of the nuchal gland contain oil as an internal phase while in the white lobules oil is the external phase and the protoplasm the internal phase. There appears to be a relation between the size and colloidal structure of the fat cells and their capacity to fix fat colored by Scarlet Red and circulating in the blood under the form of hemoconias. L. W. R.

Racial distribution of isohemagglutinin groups. J. H. LEWIS AND DEBORAH L. HENDERSON. *J. Am. Med. Assoc.* 79, 1422-4(1922).—The authors follow Jansky's blood grouping, which has been adopted by the Am. Assoc. Immunologists. Conclusions: (1) The distribution of isohemagglutinin Groups II and III among American negroes is very different from that among the white race. (2) It approximates the distribution of hemagglutinin groups among African Negroes, but differs from the latter in an increase of the percentage of Group II and a decrease of the percentage of Group III. (3) Since the difference in the distribution of the hemagglutinin groups among African and American Negroes lies in the direction of an approach to the distribution among the white race, it is assumed that the change is due to intermixt. with the latter. L. W. RIGGS

Medicolegal application of human blood grouping. R. OTTENBERG. *J. Am. Med. Assoc.* 79, 2137-9(1922).—The various technics are described and the open slide method of Vincent is given the preference. The sources of error are: (1) deteriorated serums, (2) weak serums, (3) hemolysis, (4) incubation at 37° (5) drying, (6) settling of cells, (7) microscopic observation, (8) dense cell emulsions, (9) undeveloped group characters, and (10) autoagglutination. On account of these, the following precautions must be observed: (a) Every test must be done in duplicate, using different sets of test serums. (b) Test serums must be shown to be active at the time of the tests. (c) Wherever there is the possibility of doubt, both serum and cells of the individual must be tested. (d) The cell emulsion without addn. of test serum must also be examd. Buchanan's failure to confirm the hereditary nature of the blood groups is apparently the result of errors of observation. L. W. RIGGS

Biologic mechanism of human isohemagglutination—The constitution of the blood groups and the inheritance of the agglutinogens. M. G. GICHNER. *J. Am. Med.*

Assoc. 79, 2143-5(1922).—The hypothesis that there are 2 agglutinogens and 2 agglutinins responsible for the serologic behavior of the 4 groups of human blood is in complete agreement with the results of the absorption of agglutinin from the serum of the several groups, and of the saturation of the agglutinin of the cells of the several groups, as demonstrated by Koeckert. The hypothesis that the presence of the agglutinogens is always dominant and their absence always recessive rests on observations on 885 individuals constituting 191 families. The hypothesis that the inheritance iso-agglutinogens follows the mendelian formula for a dihybrid rests on: (a) The existence of 2 different unit characters. (b) The occurrence in nature of all the genotypes to be expected from a dihybrid mating. (c) The occurrence of the phenotypes (blood groups) in the numerical proportion expected for the mating of the several genotypes.

L. W. RIGGS

Influence of diet on blood grouping. JOHN HARPER AND W. C. BYRON. *J. Am. Med. Assoc.* 79, 2222-3(1922).—Men were fed an ordinary diet, a green-free diet and a green diet, after which the agglutinating properties of their serums were tested. Using the Jansky classification, the results showed that the diet appears to influence the serum of Group III, and that both ordinary and green-free diets interfere with the proper agglutination of cells of Group III blood in Group II serum. Although the number of tests made is too limited to yield a basis for definite conclusions, it is suggested that these findings may stimulate investigation along this line.

L. W. R.

Comparison between the chemical and physiological characteristics of pepsin and rennin. FREDERIC FENGER. *J. Am. Chem. Soc.* 45, 249-55(1923).—Pepsin and rennin are proteins with widely different properties. Pepsin is coagulated by heat and is colloidal in nature, while rennin is a decompn. product of protein of the acid albumin type and is not pptd. by boiling. Pepsin can be dialyzed, while rennin diffuses freely through parchment. Proteolytic or peptic activity seems to be no part of the true physiol. characteristics of the milk-curdling enzyme; pepsin digests 25,000 times its wt. of freshly coagulated and disintegrated egg albumin in 2.5 hrs. at 52° and rennin can coagulate more than 2,000,000 times its wt. of fresh milk in 10 min. at 40°. Both enzymes are present in the stomach of the suckling calf, but only pepsin was found in that of the adult hog.

C. A. R.

Sucrase. E. CANALS. *Bull. soc. chim.* 31, 921-8(1922).—In corroboration of the theory of Tribot (*C. A.* 3, 1878), Mg and P were found in considerable quantities in 8 preps. of sucrase, while other mineral elements were variable in their presence.

J. J. WILLAMAN

Membrane equilibria (GARNER) 2. Purines (MOORE, GATEWOOD) 10.

B—METHODS AND APPARATUS

STANLEY R. BENEDICT

The clinical significance of calcium concentration in the serum of children and possible errors in the determination. B. KRAMER, F. F. TISDALL AND J. HOWLAND. *Am. J. Diseases Children* 22, 560-4(1921).—A table shows a series of Ca detns. of blood serum in normal children and adults in health and disease. The normal child has 10-11 mg. per 100 cc., the normal adult 9.7-10.8. The only changes were noted in cases of tetany and renal insufficiency, in both of which the Ca was diminished more or less distinctly. Sources of error in the micro method are pointed out. HNO_3 , $\text{CCl}_3\text{CO}_2\text{H}$ and even distd. water may contain traces of Ca. Filter paper may contain Ca in relatively large amts. Ca oxalate is not wholly insol. in water. The prepn. of Ca as the oxalate must be accomplished in the presence of both Mg and phosphates, which may become sources of error. In unwashed serum or plasma the Mg or phosphate content is small, except in some pathol. condition. Mg in serum and plasma cannot be

considered a serious source of error. The optimum p_H of the fluid for the quant. pptn. of Ca oxalate is 5.2–6.2. HCl should not be used in an analysis in which the final detn. involves a permanganate titration. S. AMBERG

Investigations on blood coagulation. II. F. WÖRLSCH. *Münch. med. Wochschr.* 68, 941–3(1921).—Attention is called to the importance of equal temp. for comparative detns. of blood coagulation. Furthermore an exactly measured amt. of blood must come in contact with an exactly defined glass surface of equal size, because the rate of production of fibrin enzyme and therefore the velocity of coagulation depends on the size of the surface wetted by blood. Eye glasses are suitable. In the tests watch glasses were used and therefore the figures are not quite exact. The coagulation time and the factor of acceleration of coagulation was detd. In 2 cases of severe hemophilia only an unimportant shortening of coagulation time was observed after raying the spleen. S. AMBERG

The rapid detection of bismuth in urine. DOMENICO GANASSINI. *Boll. chim. farm.* 61, 705–8(1922).—A reply to Dezanì (*Biochimica terap. spec.* 9, 267) who criticizes G.'s alkali stannite method for detecting Bi in urine (*C. A.* 16, 3098). Dezanì's iodide method is sensitive 1:300,000 and the stannite method 1:210,000. The lesser sensitivity of the latter is more than compensated by the fact that the method is based upon the most characteristic reaction of Bi, and is, therefore, more specific. A. W. DOX

Sterilization of albumin solutions and of albumin by means of chloroform. HUGO KÜHL. *Süddent. Apoth.-Ztg.* 62, 433(1922).—CHCl₃ is superior to Et₂O or toluene for sterilizing albumin solns. or albumin for culture media because it settles to the bottom of the container (on account of the high sp. gr.) and its vapors pass through the entire soln., whereas Et₂O and toluene evap. from the surface. Blood, for example, is sterilized as follows: The serum obtained in the usual way is shaken in a closed flask with 5% of CHCl₃ for 1/2 hr., allowed to stand for a short time, and centrifuged for about 2 mins. The soln., which is satd. with CHCl₃, is then decanted into sterile flasks. To obtain the reversible gel, the soln. is evapd. to dryness in a vacuum app. at 40°. A. G. DU MEZ

The silver iodide method of Kottmann. ERNST LAUDA. *Z. Immunität.* 34, 455–72(1922).—The Kottmann AgI method is a very useful means of detg. the degree of dispersion of serum. E. B. FINKE

The determination of the titratable alkali of the blood. ISIDOR GREENWALD AND GERTRUDE LEWMAN. *J. Biol. Chem.* 54, 263–83(1922).—The method depends upon the pptn. of the proteins and lipoids with a small excess of picric acid and the detn. of free acid and of total picric acid in the filtrate. The difference represents the amt. of picric acid in the filtrate combined with base previously combined with protein or with HCO₃ in the blood. The results are expressed in terms of cc. of 0.1 N alkali per 100 cc. blood. By a suitable choice of indicators, the *buffer value* between the end-points shown by those indicators can be detd. with considerable accuracy. Add to 5 cc. of oxalated blood, dild. with about 10 cc. H₂O, about 30 cc. 1% picric acid soln. and dil. the mixt. to 50 cc. After a few min. filter and heat 30 cc. of the filtrate to boiling, cool in ice and titrate with 0.01 N NaOH. Several indicators may be used in the same sample. Those recommended are 4 drops 0.01% methyl red (Na salt), 4 drops 0.01% phenol red (Na salt) and 8 drops 1% thymolphthalein (in EtOH with enough NaOH to give a slight blue color), each added after the preceding titration has been completed. The end-points thus obtained are at p_H 6.0, 7.4 and 9.0, resp. After acidifying with HOAc, heat the liquid to boiling and ppt. the *picric acid* by the addition, drop by drop, of a 1% soln. of *nitron* in 10% HOAc (Busch and Blume, *C. A.* 2, 1540). Filter on a Gooch crucible, wash, dry at 110° for 1 hr. and weigh. If thymolphthalein is used, subtract a correction

of 0.1 mg. for each drop of 1% soln. Picric acid titrates as a monobasic acid to methyl red but binds more alkali when phenol red or thymolphthalein is used. One mg. nitron picrate = 0.1848 cc. 0.01 *N* NaOH to methyl red, 0.1890 cc. to phenol red and 0.1958 to thymolphthalein. From the alkali equiv. of the nitron picrate subtract the amt. of alkali required to titrate the free acid to the same indicator. Divide the figure obtained by 3 and multiply by 10 to obtain the number of cc. of 0.1 *N* derived from 100 cc. of blood. The error is less than $\pm 1\%$ with methyl red and less than $\pm 25\%$ with the other indicators. With only 1.6 cc. blood, centrifuging and titrating 10 cc. of filtrate the errors are about 1% greater. With very small quantities of blood, the *picric acid* is detd. by titration with $TiCl_3$. Measure 0.3-0.5 cc. of blood from a 0.5 cc. Mohr pipet graduated to the tip at intervals of 0.01 cc. and capable of being read to 0.005 cc. into a 5-cc. centrifuge tube, which is graduated in 0.05 cc. and which contains a few drops of H_2O . Rinse the pipet with this H_2O and then with a little fresh H_2O . Add 1% picric acid soln. to make the final vol. 10 times that of the blood taken, cover the tube with a small rubber cap, shake, allow to stand a few min. and centrifuge. Remove as much as possible of the supernatant liquid with a 3-cc. Mohr pipet, graduated to the tip in 0.025 cc., and deliver into a conical flask 14 cm. high, 30 mm. in diam. at bottom and with neck 18 mm. diam., and titrate the free acid with 0.005 *N* NaOH from a 2 cc. buret, graduated in 0.01 cc. with 1 drop 0.01% methyl red as indicator. Add 20 drops concd. H_2SO_4 and insert a rubber stopper, which carries an inlet tube reaching nearly to the bottom of the flask, an exit tube and a glass plug. Pass a current of CO_2 through the flask while the contents are heated to boiling. Remove the plug and through this opening add 10 cc. of approx. 0.05 *N* $TiCl_3$, replace the plug and boil 5 min. Sufficient excess $TiCl_3$ should be present to give the soln. a pink color. Cool, remove the plug and titrate the excess of $TiCl_3$ with approx. 0.05 *N* $Fe_2(SO_4)_3$. When the titration is nearly completed, add $\frac{1}{10}$ vol. 10% NH_4CNS and continue the titration to the appearance of a red color. Do not interrupt the stream of CO_2 until the titration has been completed. The solns. are kept in bottles attached to hydrogen generators. The $Fe_2(SO_4)_3$ soln. keeps well and need be standardized against picric acid only once; the $TiCl_3$ deteriorates slowly and should be standardized daily with the $Fe_2(SO_4)_3$. 1 cc. 0.05 *N* $TiCl_3$ (or $Fe_2(SO_4)_3$) = 1/1.8 cc. 0.005 *N* alkali. The calcn. is obvious. The error is $\pm 4\%$. This method could not be applied to drop quantities of blood from the fingers apparently because the pressure required to secure the needed quantity of blood caused the admixture of tissue juice. The results are not affected by the degree of satn. of the blood with O_2 or with CO_2 , by the presence of a moderate excess of oxalate or by allowing the blood to stand several hrs. at room temp. or in the ice-chest. Added acid or alkali was quant. recovered. The values in normal human blood varied from 39.1 to 47.2, av. 44.8 cc. 0.1 *N* NaOH per 100 cc. blood to methyl red; from 33.4 to 42.6, av. 37.9 cc. to phenol red and from 25.9 to 36.7, av. 32.3 cc. to thymolphthalein. The values for dog and sheep blood were about the same. Of the total buffer value of about 11 cc. between pH 6.0 and 9.0, about 2 cc. is due to H_2PO_4 or similar compds., 3 or 4 cc. to amino acids, peptides, etc., and the remainder is unaccounted for. Expts. are reported in which acids or alkalies were injected into dogs and the CO_2 content and combining power of the plasma compared with the titratable alkali of the blood and plasma. At first, the titratable alkali diminished more slowly than did the CO_2 capacity but, after the latter had fallen to about 0.5 its normal value, the decrease in the titratable alkali to methyl red was about as much and that to thymolphthalein was even greater. Similar results were obtained in a series of pathological bloods. The detn. of the amt. of titratable alkali, to thymolphthalein, may be a very useful means of detecting acidosis.

I. GREENWALD

A system of blood analysis. Supplement IV. A revision of the method for de-

termining uric acid. OTTO FOLIN. *J. Biol. Chem.* **54**, 153-70(1922); cf. *C. A.* **16**, 1789, 2524.—A discussion of the conditions affecting the accuracy of uric acid detns. Uric acid added to sheep blood cannot always be completely recovered; losses amounting to as much as 7% occur even if in order to avoid occlusion of uric acid 0.8 of the required amt. of H_2SO_4 is added drop by drop and the rest after 20-30 min. also drop by drop. If the acid be added at once, the loss may be 3% greater. A new standard uric acid soln. is prepd. by dissolving 1 g. in 150 cc. 0.3% Li_2CO_3 soln. at 60°, cooling and dilg. to 500 cc. then adding 25 cc. 40% HCHO , 3 cc. glacial HOAc , shaking to remove most of the CO_2 and dilg. to 1000 cc. The soln. is kept in small bottles in the dark. For use in urine analysis a ten-fold, in blood analysis a 250-fold, diln. is used. A soln. prepd. by mixing 1 cc. with about 125 cc. H_2O , 10 cc. 0.67 N H_2SO_4 , 1 cc. 40% HCHO (no more) and finally dilg. to 250 cc. will keep several weeks. Benedict's arseno-phosphotungstic reagent offers few advantages over the original Folin-Denis reagent. The latter gives even less color with resorcinol than does the former, if NaCN is employed as the sole alkali. The formation of turbidities in the mixts. intended for colorimetric comparison can be prevented by the use of $\text{Li}_2\text{C}_2\text{O}_4$ instead of $\text{K}_2\text{C}_2\text{O}_4$ as an anticoagulant or by adding Li_2SO_4 during the detn. The use of oxalated cloth, prepd. by immersing starch-free "bird's eye" cotton cloth in a soln. of 10 g. Li_2CO_3 and 17 g. $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 240 cc. H_2O at 70° and drying, is recommended. NaCN solns., when freshly prepd., give a blue color with the Folin-Denis reagent but after 2 or 3 weeks, this color is no longer obtained. If so old that they are strongly ammoniacal, they must be boiled before using. The procedure now recommended is: measure 5 cc. blood filtrate and 2 cc. H_2O into a test-tube graduated at 25 cc. and 5 cc. standard soln. (=0.02 mg. uric acid) and 2 cc. H_2O into another. Add to each, 2 or 3 drops 20% Li_2SO_4 , 2 cc. 15% NaCN in 0.1 N NaOH 1 and cc. Folin-Denis reagent. Mix, let stand 2 min. and then immerse in boiling H_2O for 80 seconds. Cool, dil. to mark and compare in the colorimeter. With standard at 20 mm., readings from 10 to 40 mm. are dependable. The uric acid may be pptd. with Ag lactate. This is prepd. by dissolving 100 g. Ag lactate in 700 cc. H_2O , adding a mixt. of 100 cc. 85% lactic acid and 100 cc. 10% NaOH and finally dilg. to 1000 cc. Blood filtrates require a large excess of Ag , so 7 cc. are added to 5 cc. blood filtrate in a centrifuge tube and, after standing 1 to 2 min., without stirring or shaking, the tube is centrifuged, and the supernatant liquid is decanted. The ppt. is stirred with 1 cc. 10% NaCl in 0.1 N HCl , after which 4 cc. H_2O and the mixt. stirred again. The tube is centrifuged again and the supernatant liquid, which need not be perfectly clear, is decanted into a tube graduated at 25 cc. Into another tube, measure 5 cc. standard soln. and to each add 2 drops Li_2SO_4 , 2 cc. NaCN and 1 cc. reagent. Let stand 2 min., heat in boiling H_2O for 80 seconds, cool and complete detn. as described above. Cf. Morris and Macleod, *C. A.* **16**, 1103; Benedict, *C. A.* **16**, 2524 and following abstr.

I. GREENWALD

The determination of uric acid. STANLEY R. BENEDICT. *J. Biol. Chem.*, **54**, 233-38(1922).—Cf. preceding abstr. In human blood, heat coagulation followed by $\text{Al}(\text{OH})_3$ cream gave values for uric acid that were very little, if any, different from those obtained after pptn. with Folin-Wu reagents. The need of the careful slow pptn. is questioned. B. points out that his reagent is satisfactory, and is less apt to give turbid solns. than is the Folin-Denis reagent. If turbidity does occur, the soln. need only be dild. to 20 cc. instead of 15 cc. B. recommends the use of a 5% NaCN soln. The improvement of NaCN solns. on standing appears to be due to the formation of NH_3 , for the same result can be obtained immediately by the addition of a trace of NH_4OH . B.'s dil. uric acid standard may be preserved for at least 6 months if, after satn. with CO_2 , it is kept in a atmosphere of CO_2 (positive pressure to prevent entrance of air). The apparatus consists of a siphon bottle and a Kipp generator.

I. GREENWALD

A simple and effective laboratory apparatus for the ultrafiltration of protein-containing systems. G. GIERSA. *Biochem. Z.* **132**, 488-93(1922).—An ingenious arrangement is described in which a porous cell or membrane thimble is immersed in the colloid sol and connected with suction flask by a glass tube dipping into a test-tube in the flask. A direct modification omitting the test-tube also is described. F. S. HAMMETT

Measuring the buffer effect. G. LEHMANN. *Biochem. Z.* **133**, 30-45(1922).—To det. the degree of buffering of a soln. the change in reaction which a soln. undergoes by the addition of HCl or NaOH of a certain normality can be utilized. The degree of buffering is the ratio of the amt. of added acid or alkali to the change in p_H . The indicator method is the simplest method of measuring. When 2 solns. of different p_H are so mixed that the mixt. has a definite p_H , the amts. of the 2 solns. necessary are inversely proportional to the same amts. of HCl or NaOH of equal normality, which must be added to the original soln. in order to obtain the desired p_H . The buffer degree of solns. in which the use of indicators is not possible can be found by mixing with a known buffered soln. The buffer action of tissues can be detd. in this way.

F. S. HAMMETT

A new color test for urea and its value as a clinical test. O. WELTMANN AND H. K. BARRENSCHIEEN. *Klin. Wochschr.* **1**, 1100(1922).—When a soln. contg. urea is mixed with a few drops of a soln. of $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CHO}$ a greenish yellow color is produced that seems to be characteristic for urea. The reaction is obtained with a 0.001 molar soln. of urea. None of the other constituents of normal urine give a color with Ehrlich's aldehyde. No color is obtained with amino acids. The compn. of the colored compd. was not detd. Urea retention may be qual. demonstrated in blood serum as follows: Free the serum from protein with $\text{CCl}_3\text{CO}_2\text{H}$, mix 1 cc. of the filtrate with 2 drops of a soln. of Ehrlich's aldehyde. Normal serum gives no color. In cases of urea retention the characteristic greenish yellow color is obtained.

MILTON HANKE

Enterotropic uric acid. II. T. BRUGSCH AND J. ROTHER. *Klin. Wochschr.* **1**, 1729-30(1922).—Uric acid can be prepd. from bile as follows: 50 cc. of clear centrifuged bile are mixed with 200 cc. of H_2O and 5 cc. of 95% H_2SO_4 . The liquid is boiled for 5 min., made slightly alk. with NaOH and then acidified slightly with HOAc . The dark colored ppt. is removed by filtration. The filtrate is treated with 10 g. of NaOAc and 3 g. of NaHSO_3 , heated to boiling and then treated with 20 cc. of a 10% soln. of CuSO_4 . The ppt. so obtained is suspended in water, acidified by the addn. 1 cc. of concd. HCl and freed from Cu with H_2S . The filtrate from the CuS is concd. on the water bath. Crystals of uric acid are obtained exactly as in the case of urine. This procedure is not quant. There was obtained 200 mg. of uric acid from 1000 cc. of bladder bile and 50 mg. from 1000 cc. of fistula bile. For the colorimetric estn. of uric acid in bile, be it fistula or duodenal bile collected with the aid of a duodenal probe, the following procedure is recommended: 50 cc. of bile is treated with a few cc. of NH_3 and then with 1-2 cc. of a Salkowski-Ludwig ammoniacal silver magnesia mixt. The mixt. is set aside for several hrs. and then filtered. The well washed ppt. is suspended in H_2O , treated with HCl, the mixt. heated to boiling and the Ag removed completely with H_2S . Uric acid is estd. colorimetrically in the filtrate from the AgS after the H_2S has been removed completely by boiling. The normal enterotropic uric acid excretion in man is between 0.10 and 0.20 g. per 24 hrs. as estd. by the above method (not claimed to be quant.). On a purine-free diet the ratio of urotropic to enterotropic uric acid seems to be about 2 to 1.

MILTON HANKE

Note on Knoop's test for histidine. GEO. HUNTER. *Biochem. J.* **16**, 637-9 (1922).—A modification of Knoop's procedure (see *Beitrage* **11**, 356(1908)). An excess of bromine water is added to the test soln., and the uncombined Br is removed by washing with CHCl_3 (in a small sepg. funnel) until the CHCl_3 is no longer colored. The

soln. is transferred to a test-tube and put in a boiling water bath. The brown color due to histidine appears. (The excess of Br appears to oxidize coloring matters—such as meat ext.—so that after washing with CHCl_3 , the soln. is almost colorless. To distinguish tryptophan from histidine, one must remember that the former gives a test with Br in the cold, and the color can be extd. with AmOH ; but "the colored substance in Knoop's test is not extd. by any of the ordinary solvents and is peculiarly unaffected by reagents other than Br." Histamine gives a test similar to histidine.)

BENJAMIN HARROW

Estimation of carnosine in muscle extract—a critical study. GEO. HUNTER. *Biochem. J.* 16, 640–54(1922).—All solns. in which carnosine is to be estd. by means of the diazo reagent (diazotized sulfanilic acid in alk. soln. (cf. *C. A.* 16, 1442)) should be free from NH_4 salts, sulfides and tannic acid. CH_2O or phenols, such as thymol, should not be used as preservatives, but muscle tissue may be preserved in alc., and exts., by a layer of toluene. In ox muscle, purines are responsible for about 3% of the color value reckoned as carnosine. Probably another 2% of the color is not due to carnosine. Histidine, which may be present in muscle tissue, may be distinguished from carnosine by Knoop's test (see preceding abstr.). The carnosine content of muscle varies with the species of animal and with different members of the same species.

BENJAMIN HARROW

Method for estimating hydrophylic colloid content of expressed plant tissue fluids. ROBT. NEWTON AND R. A. GORTNER. *Bot. Gaz.* 74, 442–46(1922); cf. Gortner and Hoffman, *C. A.* 17, 409.—The f.-p. depression of the freshly expressed plant juice is first obtained. Then, having detd. the total solids by the refractometric method, a quantity of sucrose just sufficient to make a molar soln. in the total water present is added. The f.-p. depression is again detd., and is usually found to have increased more than the theoretical amt. It is assumed that the magnitude of the excess depression is a measure of the quantity of water held in such a way as to be unavailable for the soln. of the sugar. The values obtained may be calcd. to percentage "bound" water. This represents the total water of hydration of all the substances in the sap, but has been found to correspond so regularly with the content of hydrophylic colloid as to indicate a close relationship.

BENJAMIN HARROW

Comparison of pentabromoacetone method, and Salant and Wise's method for citric acid determination in urine. W. B. McCLURE AND L. W. SAUER. *Am. J. Physiol.* 62, 140–4(1922).—When known amts. of citric acid were added to normal urine the pentabromoacetone method (*C. A.* 12, 383) gave much better results than Salant and Wise's method (*C. A.* 11, 495) in 3 cases. In the fourth case there was close comparison between the results of the 2 methods. The pentabromoacetone method is preferred by the authors. Cf. *C. A.* 16, 3916.

J. F. LYMAN

Further observations on "color standards" for the colorimetric determination of hydrogen concentration. L. S. MEDALIA. *J. Bact.* 7, 589–97(1922).—Detailed requirements for the prepn. of color standards are given (cf. *C. A.* 15, 244). JOHN T. MYERS

A modified Haldane open circuit apparatus for measuring the respiratory exchange in newborn babies and also in rabbits and cats. DAVID MARINE. *J. Metabolic Research* 2, 29–37(1922). A complete description and detailed drawing of the app. are given.

W. A. PERLZWEIG

Technic of measuring the respiratory exchange (basal metabolism). M. LABBÉ AND H. STEVENIN. *Presse med.* 30, 841–3(1922).—The app. employed consists of an open system comprising a gas mask mouth-piece, a gas-mixer, a spirometer measuring the vol. of expired air, and a direct reading Lullian eudiometer giving the gas vol. after passage through KOH and P_2O_5 absorption bulbs. Methods of operation and of calcn. of results are given in detail. This app. gives results comparable in reliability with the better known American app.

W. A. PERLZWEIG

The detection and identification of maltose, galactose, saccharose and inulin by a mycological method. ALDO CASTELLANI AND F. E. TAYLOR. *J. Trop. Med.* **25**, 41-6 (1922).—An extension of the previously published method (*C. A.* **13**, 28). A table shows the reaction of a number of bacteria and fungi with a great variety of carbohydrates. Fermentation tests with two suitable microorganisms is sufficient to establish the identity of any of the sugars named in the title. Cf. *C. A.* **17**, 409. W. A. P.

D—BOTANY

B. M. DUGGAR

Flower pigments. R. SCHOLDER. *Süddeut. Aboth.-Zig.* **62**, 355-355(1922).—Review of the work of Willstätter on the anthocyan pigments. A. G. DUMÉZ

Relation between manganese and ash content in old and in young leaves. F. JADIN AND A. ASTRUC. *Bull. soc. chim.* **31**, 917-21(1922).—Mostly polemical with Bertrand and Rosenblatt (*C. A.* **15**, 4020), with some new analyses. J. J. W.

Recent investigations on carbon assimilation and the degradation of starch. R. BAECCKER. *Mikrokosmos* **15**, 220-30(1922).—Discussion of the work of Kleinstück (*C. A.* **12**, 1721) and of Molisch (*C. A.* **16**, 1448). J. J. WILLMAN

E—NUTRITION

PHILIP B. HAWK

NORMAL

Studies of infant feeding. XIII. The caseins of cow milk and human milk in their relation to infant feeding. The action of rennin on casein. A. W. BOSWORTH. *Am. J. Diseases Children* **22**, 193-201(1921); cf. *C. A.* **13**, 2696.—The data of interest here have been published elsewhere. S. AMBERG

The antiscorbutic property of fruits. An experimental study of apples and bananas. M. H. GIVENS, H. B. CLUGAGE, AND E. G. VAN HORNE. *Am. J. Diseases Children* **23**, 210-25(1922).—Raw apples and raw bananas are antiscorbutic agents. Exposure to temps. such as used for drying or canning leads to a very marked loss of antiscorbutic power. Cooking bananas 15 min. at 100° destroys this power; cooking in the presence of dil. citric acid left some intact. S. AMBERG

The importance of cysteine for cellular metabolism. EMIL ABDERHALDEN. *Arch. néerland. physiol.* **7**, 231-6(1922).—Cysteine and cystine play an important role as catalytic agents in biol. oxidations. Animals fed on a diet free from cystine exhibit marked symptoms of inanition; the exchange of O₂ of the tissues of these animals is considerably diminished. Also cases of cystineuria of 3 children of the same family, leading rapidly to inanition and death, are described. Crystals of secreted cystine were found in the tissue of these children. R. BEUTNER

The inorganic constituents of the body in avitaminosis. K. MORINAKA. *Biochem. Z.* **133**, 63-66(1922).—The H₂O content of the body of mice deprived of vitamins was found to be the same as that of normally fed mice. The ash content of the undernourished animals was higher than that of the mice which had vitamins in the diet. The ash of the mice on the deficient diet contained a higher % of Ca and Mg and a lower % of K and P. F. S. HAMMETT

The significance of vitamins in the exchanges of the animal body. I. The role of protein and carbohydrate in vitamin hunger. L. TSCHERKES. *Biochem. Z.* **133**, 75-81(1922).—Expts are reported on pigeons which indicate that the intermediary metabolism of protein and carbohydrate in the absence of vitamin takes on an aberrant character in that not only are the tissues incapable of utilizing the food but that the food is even a poison for the organism. F. S. HAMMETT

Vitamins in connection with infant feeding. E. A. BARTON. *J. State Med.* 30, 470-79(1922).—A review of the role of vitamins A and C in infant nutrition. The lack of vitamin C in infants may seriously interfere with the rudimentary second teeth. The anti-rachitic vitamin is probably identical with vitamin A. Deficiency of Ca or excess of carbohydrate may aggravate the symptoms attendant upon deficiency of vitamin A. Administration of cod-liver oil when teething is delayed is recommended.

H. B. LEWIS

The relation between the qualitative requirements of nitrogen and of accessory factors in nutrition. A. BLANCHETIÈRE. *Chimie et industrie* 7, 870-8; 8, 990-1004 (1922).—A review.

A. P. C.

Studies of the vitamins of cod liver oils. I. The potency of crude cod liver oil, pressed cod liver oil and cod liver stearin. A. D. HOLMES. *J. Metabolic Research* 2, 113-22(1922).—All of the 3 oils were obtained by the usual com. processes from the same crude oil and were tested for vitamin A content on albino rats. All 3 were found to be capable of meeting the requirements for vitamin A of growing rats. The vitamin content of the pressed oil was found to be approx. twice that of the crude oil or the stearin.

W. A. PERLZWEIG

Calorific and energy requirements in man. A. GIGON. *Presse med.* 30, 797-9 (1922).—A review.

W. A. PERLZWEIG

ABNORMAL

Antidote to the toxic effects of excess protein during lactation. GLADYS A. HARTWELL. *Lancet* 1922, II, 963-4; cf. *C. A.* 16, 735.—Excess protein (about 46% of the total solids) given to nursing rats causes spasms and ultimate death of the offspring, although the mother does not appear to suffer. Milk acts as an antidote. The protective substance in the milk is apparently vitamin B. Complete antidote effect was obtained with tomato, potato, carrot and artichoke. Other fruit and vegetable juices were less effective. Whole foods, such as wheat germ, yeast and egg yolk protected the young, egg yolk being particularly effective. These expts. indicated that any danger from excess protein in the diet of the nursing mother, in the rat at least, could be obviated by the use of a diet rich in vitamin B.

E. R. LONG

Further experiments with high fats in diabetes. F. S. LECLERCO. *J. Metabolic Research* 2, 39-54(1922); cf. *C. A.* 16, 2536.—Further evidence from clinical observation is presented showing the injurious effect of increasing the fat in diabetic diets beyond the caloric tolerance of the patient. The most obvious injury as seen by L. is that of the assimilation as expressed by a rise of the blood sugar. The polemic with Newburgh and Marsh is continued.

W. A. PERLZWEIG

Content of diastase in the pancreas of beriberi pigeons. F. ROTHLIN. *Z. physiol. Chem.* 121, 300-6(1922); cf. Hess, *C. A.* 16, 2523.—The content of diastase is the same as that of normal pigeons; its activity is unaffected by HCN.

R. L. STEHLE

F—PHYSIOLOGY

ANDREW HUNTER

Blood studies in the newborn. Morphological, chemical, coagulation, urobilin and bilirubin. W. P. LUCAS, B. F. DEARING, H. R. HOOBLE, A. COE, M. R. JONES, AND F. S. SMYTH. *Am. J. Diseases Children* 22, 525-59(1921).—The non-protein N, urea N, uric acid N, creatinine N, sugar and CO₂ per 100 cc. blood (by the method of Folin, Folin and Wu, and the CO₂ by Van Slyke) are given for the first 12 days of life. Ca in whole blood, corpuscles and plasma averaged for the 12 days, boys and girls together, 8.8, 5.0 and 12.3 mg., resp., per 100 cc. For detg. the coagulation time the blood was taken from the longitudinal sinus, placed in 2 cc. quantities in test-tubes, and the

time taken when it was possible to invert the tube without the clot slipping. During the first 4 days the coagulation time is definitely increased and during this time the prothrombin element is distinctly diminished. No urobilin or urobilinogen could be found in the stools. The bilirubin was detd. in plasma by placing 3 cc. drop by drop into a soln. made with 30 cc. concd. HCl in 2 l. 95% alc. and making up to 25 cc. On standing an emerald-green color develops, reaching its highest intensity in 24 hrs. This is compared with a wedge made of gelatin, CuSO₄ and India ink in a Hellige colorimeter, standardized with bilirubin. Of 90 cases 82 showed a positive bilirubin reaction. The av. curve begins with 5 mg. bilirubin per 100 cc. plasma, rises on the third day to 21 mg. to drop to 8 mg. on the 14th day. The individual curves do not show very much similarity with regard to quantity. The peak on about the third day seems to be fairly const.

S. AMBERG

Constant differences in the composition of the cerebrospinal fluid in different localities of the subarachnoidal space. W. WEIGELDT. *Munch. med. Wochschr.* 68, 838(1921).—The protein content of the cerebrospinal fluid is always greater in the spinal canal than in the ventricles of the brain.

S. AMBERG

The coagulation of the blood after raying of spleen and liver. F. VON DER HÜTTE. *Munch. med. Wochschr.* 68, 846-8(1921).—Stimulating raying of spleen produces in most cases a shortening of the coagulation time after an initial increase. The shortening becomes most pronounced after 4-5 hrs. and disappears latest after 8 hrs. Raying of the liver shortens the coagulation time in only 1/3 of the cases.

S. AMBERG

The relation between the changes of temperature and the consumption of oxygen by cold-blooded animals. M. N. I. DIRKEN. *Arch. néerland. physiol.* 7, 126-31(1922).—Various cold-blooded animals, especially *Periplaneta americana*, were kept in a thermostat at temps. varying from 10° to 25°. The consumption of O₂ was measured by absorbing the CO₂ formed with NaOH. The consumption does not increase regularly with the temp. according to the rule of van't Hoff, but it is subject to nervous impulses which vary with the temp. in a complicated manner.

R. BEUTNER

The tension and the consumption of oxygen in the aqueous humor. J. DE HAAN. *Arch. néerland. physiol.* 7, 245-50(1922).—The O₂ content of the fluid contained in the eye of a rabbit is detd. by the micromethod of Krogh (*Handbuch biolog. Arbeitsmethoden*, Abt. IV, 10, 179(1920)). With 7 different rabbits values varying between 18 and 26 mm. Hg are found. Since, however, a considerable consumption of O₂ takes place during the analysis, all these values are likely to be too small. The consumption of O₂ during this space of time is detd. and, after adding the O₂ consumed, 40 mm. Hg is found to be the real O₂ content of the fluid. This is about the same value as that for venous blood.

R. BEUTNER

Chemistry of the liver. U. SAMMARTINO. *Biochem. Z.* 132, 343-51(1922).—The most important fact in this study is the finding of the presence of notable amts. of free fatty acids in the unsapond. exts. of liver pulp accompanying the glycerol and cholesterol fats. The assumption is that the fats were split in the intestine, or that but a small portion is split, the rest being directly absorbed as fine particles. The first assumption appears the more probable.

F. S. HAMMETT

The ion exchange between the blood corpuscles and the serum. K. MEIER. *Klin. Wochschr.* 1, 1748(1922).—The ion exchange between the corpuscles and the serum is dependent to a very large extent upon the reaction of the blood. If whole blood is satd. with CO₂ under varying pressures, and the corpuscles are sepd. from the serum, the CO₂-holding capacity of the serum and its alkali content are found to be markedly increased with increasing concns. of CO₂. Simultaneously, the chloride content of the serum decreases and of the corpuscles increases. The increase in the alkali content of the serum is greater than can be accounted for by the loss in chloride which

is probably due to a migration of alkali from the corpuscles into the serum. The water content of the serum decreases and of the corpuscles increases. MILTON HANKE

The distribution of sugar, non-protein nitrogen and calcium in blood. J. K. PARNAS AND W. V. JASINSKI. *Klin. Wochschr.* 1, 2029-30(1922).—Genuine plasma has a glucose content identical with that of oxalated or citrated plasma. The erythrocytes, whose vol. is 42-43% of the total blood, contain 85-100% as much sugar as the plasma. The non-protein N content of genuine plasma is identical with that of the oxalated or citrated plasma. The erythrocytes contain as much non-protein N as the plasma, or slightly less. The Ca content of the erythrocytes is 7.5-8% that of the plasma. The expts. were conducted upon healthy young men with a blood sugar value of 0.097 to 0.1125%.

MILTON HANKE

A discussion of the method of A. D. Waller for computing energy output and results of experiments determining energy expenditure during some household tasks. S. GARNES AND M. K. O'BRIEN. *J. Ind. Hyg.* 4, 233-91(1922).—Waller's method of computing energy output from the CO_2 expired involves serious errors in the short periods used for collecting samples and in the method of sampling of the expired air. His method for the detn. of the efficiency of a subject also is inaccurate because it does not take into consideration the caloric output. The av. cost in cal. per hr. per sq. m. was as follows for various household tasks: (1) bread-making, 33.53 cal. with av. variation of ± 13.52 cal. (8 expts.); (2) machining, 1605 cal. ± 9.72 cal. (10 expts.); (3) floor polishing, 48.86 cal. ± 25.06 cal. (11 expts.).

H. B. LEWIS

A note on the "ammonia coefficient" in menstruation. MURIEL BOND. *Lancet* 1922, II, 957.—Observations on the compn. of the urine of a normal subject indicated a relationship between the value of the "ammonia coeff." and menstruation. In the post- and intermenstrual periods the coeff. varies slightly from the intermenstrual av., but in the 7 days previous to the period, i. e., the premenstrual period, there is a marked rise. This rise appears due to a rise in the total output of urinary ammonia, rather than to a decrease in the total urinary N.

E. R. LONG

The excretion of chlorides and bicarbonates by the human kidney. H. W. DAVIES, J. B. S. HALDANE AND G. L. PESKETT. *J. Physiol.* 56, 260-74(1922).—The max. possible mol. concn. of chlorides in the urine is definite for the individual (0.33 N for J. B. S. H.). The max. for bicarbonates has the same value. When chlorides and bicarbonates are being excreted together the max. possible sum of their mol. concns. has this same value. This max. is independent, within wide limits, of the total mol. concn. of the urine, of those of urea and phosphates. Chlorides and bicarbonates must be concd. by the same part of the kidneys, which is probably resorptive; urea and phosphates are concd. by a different one, which is excretory.

J. F. LYMAN

Anoxemia and the administration of oxygen. N. MORRIS. *J. Physiol.* 56, 283-93 (1922).—The O_2 satn. of arterial and venous blood was detd. in rabbits before and after the production of anoxemia. Interference with respiration (by unilateral pneumothorax, occlusion of one bronchus, pneumococcal infection or histamine injections) lowers the O_2 content of the arterial blood. The "head of O_2 " i. e., % of O_2 satn. of arterial — % of O_2 satn. of venous blood, is not a const. but depends on the degree of pulmonary ventilation among other factors. Administration of O_2 subsequent to interference with the pulmonary mechanism raises the O_2 satn. of the arterial blood to normal. O_2 administration antecedent to the induction of pneumothorax and continued thereafter prevents any fall in the O_2 satn. of the arterial blood. J. F. LYMAN

The oxygen consumption during running. A. V. HILL AND H. LUPTON. *Proc. Physiol. Soc., J. Physiol.* 56, xxxii(1922).— O_2 consumption while running at 6.4 to 7.6 miles per hr. (man with Douglas bag) was steady, i. e., the energy expended was accounted for by O_2 absorbed. At greater speed (9.1 to 10 miles per hr.) more energy

was used than was accounted for by O_2 consumption, i. e., the subject was going into debt for O_2 . The most severe exercise possible (about 70 times the basal metabolic rate) led in 10 secs. to a total O_2 deficit of about 2500 cc. and in 20 secs. to about 5500 cc. Such O_2 debts cannot be endured long because a stage is soon reached at which the accumulation of unoxidized lactic acid prevents further effort.

J. F. LYMAN

Morphine hyperglucemia and the adrenals. G. N. STEWART AND J. M. ROGOFF. *Am. J. Physiol.* 62, 93-112(1922).—Hyperglucemia produced by morphine appears to depend in some way on adrenal action since the occurrence of a definite hyperglucemia is far more const. when the adrenals have not been interfered with than after the various adrenal operations practised by S. and R. The authors consider that morphine hyperglucemia in normal animals is not an "adrenaline hyperglucemia" due to the stimulating effect of the drug upon adrenaline output. It may, however, be facilitated by the ordinary output of adrenaline.

J. F. LYMAN

The effect of pancreatic extract (insulin) on normal rabbits. F. G. BANTING, C. H. BEST, J. B. COLLIP, J. J. R. MACLEOD AND E. C. NOBLE. *Am. J. Physiol.* 62, 162-76(1922).—(1) Insulin (*C. A.* 16, 3115) injected subcutaneously into normal rabbits causes a fall in the % of blood sugar within a few hrs. (2) As the blood sugar falls the rabbit exhibits signs of hunger and thirst, hyperexcitability and apparent fear. (3) The animal may recover from these earlier symptoms but frequently the hyperexcitability becomes extreme and clonic convulsive seizures involving the entire body and lasting several mins. supervene. (4) In the great majority of cases exhibiting convulsions the blood sugar has been found to be about 0.045%. (5) Subcutaneous injections of dextrose antidote the convulsions and other symptoms. (6) A peculiar mucigenous degeneration of the subcutaneous tissues of the abdominal wall is very commonly observed in animals that die as a result of the symptoms. (7) As a basis for the physiol. assay of insulin the authors suggest as one unit the number of cc. which cause the blood sugar of normal rabbits to fall to 0.045% within 4 hrs. This dose is decidedly active in lowering blood sugar in diabetic patients.

J. F. LYMAN

Effect of insulin (pancreatic extract) on the sugar consumption of the isolated surviving rabbit heart. J. HEPBURN AND J. K. LATCHFORD. *Am. J. Physiol.* 62, 177-84(1922).—Insulin (*C. A.* 16, 3115) added to the perfusion fluid (Locke's soln.) passing through an isolated beating rabbit heart increased the dextrose consumption from 0.87 mg. per g. per hr. to 3.06 mg. per g. per hr.

J. F. LYMAN

Vascular reaction to adrenaline in perfusates of various hydrogen-ion concentration. II. The portal-venous system of the liver. C. D. SNYDER AND L. E. MARTIN. *Am. J. Physiol.* 62, 185-91(1922).—When the terrapin liver is perfused with saline solns. of various p_H the additions of min. amts. of adrenaline ($1:10^6$) to the perfusate increase or decrease the rate of outflow from the hepatic veins depending on the acidity of the perfused soln. With the C_H of a perfusing fluid set somewhat above that of the vascular blood, adrenaline in min. effective doses is an inhibiting or depressor agent. With the C_H somewhat below that of the blood adrenaline in the same min. dosages still has the exciting or pressor action that is observed invariably for larger doses.

J. F. LYMAN

The thyroid apparatus. VII. A differential effect of thyroparathyroidectomy and parathyroidectomy on the incisor teeth of the albino rat. F. S. HAMMETT. *Am. J. Physiol.* 62, 197-201(1922); cf. *C. A.* 16, 2539.—After removal of the parathyroids in albino rats various types and degrees of dental defects occur. The more serious disturbances may show themselves as a kind of overgrowth, particularly of the upper incisors. After removal of both thyroids and parathyroids the teeth remain normal to all outward appearances. Parathyroid function appears to be connected in some way with Ca metabolism.

J. F. LYMAN

The liberation of adrenaline during muscular exercise. F. A. HARTMAN, R. H. WHITE AND H. A. MCCORDOCK. *Am. J. Physiol.* **62**, 225-41(1922); cf. C. A. **16**, 3948.—Adrenaline output was detd. in the cat by the increased dilatation of a denervated pupil (superior cervical ganglion removed). Exercise causes increased adrenaline output in the cat, with a latent period less than 1.5 to 3 mins. Increased output of adrenaline persists after vigorous exercise for varying periods. J. F. LYMAN

The secretion by the isolated kidney. E. B. VERNEY AND E. H. STARLING. *J. Physiol.* **56**, 353-8(1922).—The mammalian kidney perfused with blood from a heart-lung prepn. is capable of secreting urine in considerable amts. The rate of secretion and rate of blood flow through the kidney vary directly with blood pressure. Under about 40 mm. Hg pressure secretion stopped. The urine secreted was invariably hypotonic to the blood serum and alk. in reaction. It is thought this may have been due to over-ventilation of the lungs, resulting in lowered alk. reserve and retention of Cl in the blood. J. F. LYMAN

The recovery heat production in muscle. W. HARTREY AND A. V. HILL. *J. Physiol.* **56**, 367-81(1922); cf. C. A. **16**, 2900.—Earlier expts. (C. A. **7**, 2605) were repeated using improved app. In O_2 , the heat produced by a muscle during recovery after activity is about 1.5 times the total initial heat production, the whole process lasting about 10 min. at 20° . In N_2 there is a much smaller but definite heat production during the recovery process, amounting to about 0.5 times the initial heat produced. Treatment of the muscle with KCN in an atm. of N_2 somewhat diminishes but does not abolish this delayed anaerobic heat. The effect of temp. on heat production during recovery shows that the velocity of the process is controlled by that of some chem. reaction. It is concluded that (1) the anaerobic and oxidative processes are of different characters; (2) recovery takes place in at least 2 stages; and (3) recovery rate is governed by that of some unknown bimol. chem. reaction; (4) in the oxidative removal of lactic acid, from 0.2 to 0.16 of the lactic acid is burnt, the remainder being restored as glycogen. The total initial heat production is about 285 cal. per g. of lactic acid set free, corresponding to the heat evolved in the production of lactic acid from glycogen, and its neutralization chiefly by the alk. protein buffers of the muscle. The production of acid leads to a rise of muscle tension, its neutralization to relaxation. J. F. L.

The catalytic effect of light upon the stability of the colloids of human blood plasma. W. STARLINGER. *Wiener klin. Wochschr.* **35**, 860-2(1922).—Citratd human plasma contg. a catalyzer (eosin or $FeSO_4$) in soln. when exposed to direct or diffuse sunlight for varying periods of time showed a distinct diminution of the precipitability of its fibrinogen. The same was shown by solns. of serum globulin and albumin after exposure to light in the presence of a catalyzer. The effect of the light is inversely proportional to its wave length, red light having no effect, while blue gives the greatest effect. Plasma in which flocculation of fibrinogen had occurred on standing showed a partial resolution of the pptd. fibrinogen upon exposure to light in the presence of a catalyzer. The phenomenon is interpreted as a hydrolytic process affecting the more coarsely dispersed colloids of the blood, rendering them more highly dispersed and hence more stable. W. A. PERLZWEIG

The significance of the lability of colloids in the blood. J. VON DARANYI. *Wiener klin. Wochschr.* **35**, 885-6(1922).—Under the term of *colloid-lability* D. sums up the changes occurring in various pathol. conditions in the quant. relationships of the blood proteins. The increase of globulins at the expense of the serum albumin in disease is a phase of colloid lability in which the colloidal system of the blood serum becomes less stable because of a predominance of the more coarsely dispersed globulins. D.'s test (*Deut. med. Wochschr.* **1922**, No. 17) consisting of the pptn. of the globulins in 0.2 cc. of serum with dil. alc. is claimed to be more sensitive and practical in detecting changes in the lability of serum colloids in tuberculosis, syphilis, etc. W. A. P.

C—PATHOLOGY

H. GIDGON WELLS

The problem of cyanosis and the conception of a "Pneumonosis" (Brauer). J. SCHJERNING. *Beitr. klin. Tuberkulose* 50, 96-120(1922).—The primary and secondary causes of cyanosis are discussed. Among the secondary causes is included degenerative changes in the respiratory surface ("Pneumonose" (Brauer)). Chloramine and urethan are unsuitable for this study in cats. O was detd. with the Barcroft app. according to Franz Müller (Abderhalden, E., *Handb. d. Biochem. Arbeitsmeth.* III). Urethan alone caused a decreased O content of arterial blood. Decerebrated cats did not live long enough, so dogs and local anesthesia were used but did not prove entirely satisfactory; for even though histologically an edema was found the alveolar epithelium revealed no changes. Cl inhalations were then utilized in cats and dogs. It was found difficult to regulate the dosage so that an O decrease occurred without fatal pulmonary edema resulting. Finally morphine was used in dogs to prevent a compensatory dyspnea. The morphine prevented accelerated respiration and a definite decrease of the O content of arterial blood after Cl inhalation attained. It is concluded that changes can occur in the lungs, not visible microscopically, but capable of altering O permeability. The aim of the expts. was to det. whether a degenerative destruction of the alveolar epithelium in the sense of "Pneumonose Brauer" can inhibit the O diffusion so that a decreased content of the arterial blood can occur, revealed in man as a cyanosis. S. believes this was achieved in dogs. Further expts. are contemplated.

H. J. CORPER

The protein in urine in amyloidosis of the kidney and Bright's disease. U. SAMMARTINO. *Biochem. Z.* 133, 85-88(1922).—The detn. of the amino acids according to Van Slyke gave the following corrected values for protein from Bright's disease and from amyloid kidney, resp.: total N 16.41, 15.60; NH_3 N 7.79, 8.78; melanin N 2.72, 3.19; arginine N 11.72, 10.77; histidine N 4.15, 4.78; cystine N 0.08, 0.33; lysine N 14.32, 12.12; amino N of the filtrate 58.40, 60.63; and non-amino N of the filtrate (proline, hydroxyproline, $\frac{1}{2}$ tryptophan) 1.94, 0.79%.

F. S. HAMMETT

The use of hypertonic glucose solutions in organic heart diseases. (Experimental and clinical.) F. KIEWITZ AND R. KIRCHHEIM. *Klin. Wochschr.* 1, 1397-9(1922).—Surviving rabbit hearts were transfused with a Ringer soln. Contraction tracings were recorded on a kymograph. The introduction of 0.5 cc. of a 30% glucose soln. increased the contraction range of normal hearts, and increased the rate of flow of the perfusion liquid under const. pressure. The introduction of 0.5 cc. of a 30% levulose soln. had a similar though less marked and less const. effect. A hypertonic salt soln. has no beneficial action on the normal heart. An entirely similar series of expts. were performed on the hearts of rabbits that had been poisoned with P. The hearts could not be revived readily; they were easily fatigued; and were not influenced in any way by the hypertonic glucose soln.

MILTON HANKE

The calcium treatment of tetany is an acid therapy. P. GYÖRGY. *Klin. Wochschr.* 1, 1399-1401(1922).—The ingestion of 5 g. of CaCl_2 leads to an increased urinary excretion of NH_3 and the acid phosphates, an increase in the p_H of the urine and a slight increase in the total urinary phosphates. The urine picture is very similar to that obtained after the ingestion of HCl or NH_4Cl and is suggestive of an acidosis. The ingestion of 5 g. of Ca lactate leads to the excretion of a urine that is suggestive of an alkalosis. Symptoms of tetany that have been attributed to a Ca deficiency, can be removed not only by the ingestion of CaCl_2 , but also by the ingestion of HCl or NH_4Cl . Ca lactate has never proved very efficient in the treatment of tetany. The customary CaCl_2 treatment is really an acid therapy and can be advantageously replaced by the more agreeable and equally efficient NH_4Cl therapy.

MILTON HANKE

The nature of heterogenetic precipitins. E. FRIEDBERGER AND A. LASNITZKE. *Klin. Wochschr.* 1, 1607-8(1922).—A rabbit was immunized to beef serum. The antiserum so obtained contained precipitins for both beef and horse serum. When both the antiserum and the beef serum were extd. with ether previous to the precipitin reaction, a flocculation was obtained just as before. If, however, the antiserum and the horse serum were extd. with ether previous to the test, no flocculation was obtained. When either the antiserum or the horse serum was extd. with ether previous to the test, less ppt. was obtained than in the unextd. couple. Extn. of the antiserum alone reduced the pptn. more than extn. of the horse serum alone. The heterogenetic precipitins are apparently lipid in character and are different from the true precipitins.

MILTON HANKE

Theoretical and practical contribution to the serodiagnosis of syphilis. CARL BRUCK. *Klin. Wochschr.* 1, 1656-7(1922).—The diagnostic syphilis reactions are not dependent upon an interaction between antibody and lipoids, or upon a primary precipitation of constituents of the serum or extractives, but consist of a mech. agglutination of very finely divided lipid particles that is stimulated by certain constituents of the luetic sera. This agglutination is rendered visible indirectly by complement absorption (Wassermann reaction), or directly by the reaction of Sachs-Georgi.

MILTON HANKE

The changes in the cholesterol concentration of the blood in cases of cholelithiasis. MARIE V. BABARCY. *Klin. Wochschr.* 1, 1828-30(1922).—Cholesterol was detd. by the method of Bloor. The cholesterol concn. of the blood is normal in the intervals between attacks. The value increases immediately after the onset of an attack and remains high for about one week. This elevation in the cholesterol concn. of the blood is so characteristic of this condition that this method can be used in the differential diagnosis between cholelithiasis and related periodically appearing disturbances such as ulcus ventriculi.

MILTON HANKE

The balance and intermediary water and salt metabolism and its relation to the serum proteins. W. NONNENBRUCH. *Klin. Wochschr.* 1, 2046(1922).—NaCl-deficient foods, sweating and diuretics lead to a loss in H_2O and NaCl and the establishment of a subnormal level which can be raised to a normal level only by the simultaneous ingestion of NaCl and H_2O . Excessive ingestion of NaCl and H_2O will not raise the level under normal conditions but may lead to edema in certain pathol. conditions, such as cachexia, neuropathy, or undernourishment. The ingestion of salt by normals leads to a loss of H_2O (the body wt. may decrease 5 kg.) but sufficient salt is retained so that the subsequent ingestion of water alone will reestablish the normal level. Under these conditions there is usually no change in the erythrocyte count; but the concn. of serum proteins is markedly increased, which may be attributed to a migration of protein from the tissues into the blood stream.

MILTON HANKE

Changes in the chemical composition of the blood after the ingestion of salt solutions by normals and by diabetics. W. ARNOLDS AND S. EYTINGER. *Klin. Wochschr.* 1, 2082-4(1922).—The blood of normals and of diabetics were examd. for sugar, NaCl, and protein, before and after the ingestion of 200 cc. of a 2% soln. of Na_2SO_4 , Na citrate and $NaHCO_3$. The alveolar CO_2 tension was also detd. in all cases. After the ingestion of 200 cc. of hot water by diabetics, the blood showed a change in sugar content from 0.30% to (a) 0.277% after 30 min. and (b) 0.276 after 60 min.; in NaCl content from 0.46 to (a) 0.525 and (b) 0.490%; and in protein from 8.12 to (a) 7.63 and (b) 7.65%. The alveolar CO_2 tension dropped from 35 mm. Hg to 31 mm. Hg 13 min. after the ingestion of H_2O and rose again to 35 mm. Hg within the following 13 min. The following changes were noted in the blood after the ingestion of 200 cc. of one of the 2% salt solns. listed above.

		Before salt ingestion.	After salt ingestion.	
			30 min.	60 min.
Sugar	Normal	0.053%	0.071%	0.103%
	Diabetic	0.162%	0.091%	0.073%
NaCl	Normal	0.600%	0.744%	0.902%
	Diabetic	0.644%	0.475%	0.458%

The concn. of serum protein and alveolar CO_2 is also slightly reduced, in diabetics, after the ingestion of salt. The CO_2 tension changed from 42 to 36 mm. Hg in the course of 40 min.

MILTON HANKE

The effect of ions upon agglutination. TAKUJI SHIONOYA. *Lancet* 1922, II, 905-7.—A salt-free agglutinin-bacteria (typhoid) combination was prepd. by repeated washing of the sediment of a mixt. of the bacteria and agglutinating serum, and subsequent dialysis. One drop of the suspension thus prepd. was added to various salt solns. and agglutination of the agglutinin-bacteria adsorption complex observed. As the common simple salts are not suitable, owing to hydrolysis and other causes, for testing the effect of ions, the Co complexes of valency 1-6 were used. The higher the valency of the cation (from 1 to 6) increased, the less became the limiting concn. with which agglutination took place; such a close relation exists that when a logarithmic curve of the limiting values and of valencies is plotted a straight line results. The pptg. action of the agglutinin-bacteria combination is entirely in accordance with the valency rule, and the combination, which may be pptd. by the action of ions, is a colloid bearing negative elec. charges.

E. R. LONG

The influence of saturnine compounds on cell growth, with special reference to the treatment of malignant neoplasms. W. B. BELL. *Lancet* 1922, II, 1005.—Pb enters into combination, probably chem., with lecithin. Pb affects those normal tissues of the body in which lecithin or similar lipius are present in greatest quantity. Malignant neoplasms contain lecithin in direct proportion to their rate of growth. Intravenous injections of a colloidal prepn. of Pb, while not without danger, can with experience be so regulated that little or no disturbance is caused. After such injection Pb can be recovered from the malignant growth in quantities proportionally greater than that in the rest of the body. In suitable doses Pb appears to arrest the growth of malignant tumors; in some cases disappearance of the neoplasm may result. Treatment of 50 cases of malignant tumor is recorded; 21 of these died from the malignant process or intercurrent disease; the majority of the rest showed improvement.

E. R. LONG

The colloidal gold reaction in neurosyphilis and other diseases of the central nervous system. CECIL WORSTER-DROUGHTY, H. J. B. FRY AND G. ROCHE LYNCH. *Lancet* 1922, II, 1063-5.—The following conclusions are drawn from 300 observations on the colloidal Au reaction in the cerebrospinal fluid. A positive Au reaction is definite evidence of org. nervous disease. In syphilis of the central nervous system a positive colloidal Au reaction appears at an earlier date than the Wassermann reaction. Although dementia paralytica is usually associated with a parietic type of curve and tabes dorsalis with a luetic type, definite exceptions occur; it is probable that the type of curve varies with the intensity of the infection of the central nervous system rather than the clinical type of disease. Antisyphilitic treatment along modern lines tends to modify and even abolish a positive colloidal Au curve. Disseminated sclerosis is associated with a positive curve, the type of which varies with the intensity and stage of the disease.

E. R. LONG

The internal secretion of the pancreas and its application to the treatment of diabetes mellitus. R. L. M. WALLIS. *Lancet* 1922, II, 1158-61.—A detailed study of several hundred cases led to the following conclusions concerning diabetes and glucosuria: it is practically confined to those who consume large quantities of fats

and carbohydrates; the glucosuria shows hourly variations, being almost negligible in the morning and gradually increasing toward night, the tolerance to sugar decreasing correspondingly, and being much reduced for 2 hrs. after a meal; the glucosuria yields readily to treatment if all the carbohydrates are consumed before midday; starvation treatment is unnecessary. An alc. ext. of the pancreas was used therapeutically; it was believed to contain the active principle from the islets of Langerhans. Fresh pancreas from a pig starved 24 hrs. before death is freed from fat and connective tissue and heated to 60° in alc. for 1 hr. The extn. is continued *in vacuo*. After about 30 hrs. a dark product is obtained, which is filtered under reduced pressure. The filtrate contains the active principle plus certain lipoids. It is evapd. down in the elec. oven at 100° to a brown hard mass, which can be easily pulverized. It is kept sealed on ice. The yield from 12 lbs. of pancreas is 70–80 g. It is water-sol. It contains polypeptides, but no proteins or peptone, and no cholesterol. It does not give reactions for histidine, bistamine or cystine. The most remarkable feature is the sensitivity to alkalis, the merest trace being sufficient to produce destruction of the active principle; on the other hand it is remarkably stable in the presence of 0.2% HCl. The ext. is glucolytic *in vitro*. When given by mouth in 3–12-gr. doses it is capable of reducing the blood sugar in certain cases of diabetes mellitus, the patients tolerance to carbohydrates being at the same time increased.

E. R. LONG

The urea content of the cerebrospinal fluid, with special reference to the diagnosis of uremia in infants. J. S. ANDERSON. *Lancet* 1922, II, 1221–2.—A fatal case of nephritis and uremia in a 2-yr.-old child is described, in which the urea reached a value of 602 mg. per 100 cc. in the cerebrospinal fluid and 710 mg. in the blood. Where it is impossible to obtain sufficient blood for analytical purposes, as in infants, recourse may be had to the spinal fluid, which is more readily obtained.

E. R. LONG

The influence of the site of injection of the antigen on the production of agglutinin. R. YAMAMOTO. *J. Osaka Med. Soc.* 21, No. 3(1922); *Japan Med. World* 2, 263.—Y. found that in the rabbit and guinea pig the largest quantity of agglutinin was produced by the injection of the antigen into the parenchyma of the testicle. The optimal production of agglutinin takes place in the intratesticular injection in 6–9 days, in the intravenous in 7–9 days and in the hypodermic injection in 11–13 days.

M. E. M.

Hemolysis in the colostrum. S. NAKAMURA. *J. Ped.* No. 264(1922); *Japan Med. World* 2, 267.—Colostrum does not develop any hemolytic action. It contains hemolytic complement which is present in the whey.

M. E. MAVER

Double refracting lipid in the urine in beriberi. S. HIRAI. *J. Japn. Military Med. Assoc.* No. 112(1922); *Japan Med. World* 2, 268.—H. tried to find the doubly refracting lipid by the use of the polarimeter. The results were positive in 11 out of 21 cases. In the examn. of the urine in cases of nephritis and P poisoning, which he studied as control, he found that 57% were positive in chronic and sub-chronic nephritis, negative in acute nephritis and remarkably positive in P poisoning.

M. E. M.

Theory of syphilis serology. The electrical charge of lipoids in aqueous dispersions and the relation of the charge to other physical conditions of lipid dispersoids. E. ERSTLIN, F. PAUL AND K. LORENZ. *Kolloid Z.* 31, 182–95(1922); cf. *C. A.* 16, 1459, 2734.—The investigation is a continuation of transport expts. carried out to det. the charge of the lipoids as they occur in exts. used for the Wassermann reaction. For these detns. an ext. as required for the Meinicke reaction was used. Dry horse heart powder is first washed with ether and then the lipoids are extd. with alc. The ext. was found to consist of "organ-lecithin" with a small amt. of cephalin admixed. *Meinicke reaction*.—1st method: 0.2 cc. of the serum to be examd. is added to 0.8 cc. of the ext. properly dild. with distd. water and then incubated for 24 hrs. at 37°. From 2 to 3% NaCl soln. is then added. After standing for one hr. in the incubator in case

of normal serum the flocks have dissolved but in case of positive lues serum they remain. 2nd method: 0.2 cc. of the serum is mixed with 0.8 cc. of the ext. which was dild. with 2 to 3% NaCl soln. After 24 hrs. in the incubator at 37° the positive lues sera show flocculation and the negative sera are clear. The authors develop a theory of elec. pptn. and test its correctness with migration expts. employing a U tube of the type used by Linder and Picton. The lipoids, whether dialyzed or not, migrated distinctly to the anode, whereby a negative charge is proved. The horse heart ext. was dild. and the expts. were carried out with 300 v. Detn. of the dry matter contained in the 2 electrode legs of the tube gave the ratio 1.6:1. In the anode compartment by employing the original ext. for the migration expt. acidity developed and in the cathode side of the tube alk. To rule out electrolytic effects, the authors dialyzed the lipid solns. and after 4 hrs. they found in the anode compartment 1.63:1 parts, after 6 hrs. 2.33:1, after 9 hrs. 4.2:1 and after 12 hrs. 8.2:1 parts. Pptn. can be obtained as in the Meinicke reaction with lues serum in 3% NaCl soln. if the lipid soln. is dialyzed completely free of electrolyte. At the end of a migration expt. of a dialyzed lipid soln. in the anode leg of the tube gives the Meinicke reaction as strong as the original ext. but the soln. from the cathode compartment does not react at all. The authors discuss and refute criticisms made and in general their exptl. methods are so conducted that the principal objections are satisfactorily met. Their final conclusions are that negatively charged lipoids in 2-3% NaCl solns. and with the addn. of lues serum produces flocculation whereas with normal serum the mixt. remains clear. A. M.

Medical inspection of lead-working factories. F. HEIM AND R. HEIM DE BALSAC. *Chimie et industrie* 8, 921-5(1922).—The presence of red corpuscles with basophilic granulations is the surest indication of *latent saturnism*: its early appearance (it generally appears before all other symptoms), frequency and ease of detection make it particularly valuable for the diagnosis of the disease. Other symptoms (mononucleosis, anemia, nucleated red corpuscles, red corpuscles with basophilic protoplasm) are of little or no value when considered alone. Analysis of *blood* of patients suffering from latent saturnism showed either absence or mere traces of Pb, so that in a normal subject with 5-6 l. of blood, the latter should contain less than 1 g. of Pb. Presence of Pb in the urine is a sure symptom of saturnism. Analyses of the urine of over 100 subjects who could not have been suffering from saturnism in any degree showed no trace of Pb (method sensitive to 0.01 mg. in 250 cc. of urine). The method consisted essentially in destroying the org. matter, and estg. the Pb colorimetrically by means of Trillat's reagent (tetramethyl base of diphenylmethane). The authors are working on an electrolytic method which will not require destruction of the org. matter. A. P.-C.

The importance of liver disturbances in the pathogenesis of *arsphenamine erythemas*. DESAUX, BEAUXIS-LAGRAVE, BOUTELIER AND BARBIER. *Presse med.* 30, 668-9(1922).—In a number of cases of post-arsphenamine erythema the authors found disturbances of bile function as shown by the excretion of bile pigments and acids in the urine, and a disturbance of the ureogenic function of the liver shown by a diminution of urea concn. in the blood and in the urine associated with acidosis with ketonemia and ketonuria. No definite theory is offered to explain satisfactorily these findings. W. A. PERLZWEIG

The role and the significance of certain acetogenic microorganisms isolated from diabetic stools. P. PAGNIEZ. *Presse med.* 30, 669-70(1922).—A review of the work of A. Berthelot (*C. A.* 16, 269) and a discussion of the possible bacterial etiology of diabetes. W. A. PERLZWEIG

Basal metabolism in retarded growth of children. NOBECOURT AND H. JANET. *Presse med.* 30, 741(1922).—Detn. of basal metabolism may disclose thyroid insufficiency

in cases of retarded growth of children, which insufficiency may otherwise be overlooked or doubted.

W. A. PERLZWEIG

Permeability and absorptive power of articular walls in pathological state. DRAGONESCO AND A. LISSIEVICI-DRAGONESCO. *Presse med.* 30, 745-6(1922).—The walls of synovial cavities were found to be less permeable to neoarsphenamine than to Na salicylate, methylene blue or to KI, when these substances were injected into the joints of arthritic and rheumatic patients and the elimination through the urine was observed.

W. A. PERLZWEIG

Protein treatment of certain cases of pernicious anemia and its pathogenesis. KNUT FABER. *Presse med.* 30, 873-6(1922).

W. A. PERLZWEIG

The pathology of the respiratory gas exchange. R. LIEBESNY AND H. SCHWARTZ. *Wiener klin. Wochschr.* 35, 879-83(1922).—Report of studies of the basal metabolism in hyperthyroidism, hypothyroidism, obesity, anemias, etc. Krogh's recording spirometer (*C. A.* 16, 4231), was used. The findings corroborate those of the American investigators in the same field.

W. A. PERLZWEIG

The stability of bacterial suspensions. IV. The combination of antigen and antibody at different hydrogen-ion concentrations. P. H. DE KRUIFF AND J. H. NORTHROP. *J. Gen. Physiol.* 5, 127-38(1922); cf. *C. A.* 16, 3696.—The amt. of immune body necessary to agglutinate a suspension of *Bacillus typhosus* increases in direct proportion to the concn. of the suspension. The amt. combined with the organisms between pH 9 and 3.7 is const. The addn. of immune serum to the bacterial suspensions at pH 2.5 increases the positive charge of the organisms. These results indicate that the combination between organism and agglutinin (or protein) is not due to opposite elec. charges, but that the effect on the charge is the result of the combination. The immune body forms a film on the surface of the organism. V. The removal of antibody from sensitized organisms. *Ibid* 139-42.—Removal of antibody from *B. typhosus* is more complete at pH 3 than pH 7. Approx. 12 agglutinating doses are firmly combined with the organisms; the excess is easily removed with distd. water. A method is described of testing for immune body on the organism which depends on the difference in the acid agglutination of sensitized and unsensitized organisms. All the immune body may be removed from sensitized bacteria by repeated washing with distd. H_2O .

CHAS. H. RICHARDSON

Diffusibility as a factor in pathology. A. CHAUFFARD, BRODIN AND GRIGAUT. *Annales de médecine* 12, 257(1922); *J. Am. Med. Assoc.* 79, 2119.—The comparative liquid diffusion of $CO(NH_2)_2$, NaCl, Na urate and glucose through a parchment membrane can be represented by the figures 93, 92, 74, and 59, resp. The comparative speed of the dialysis and the difference in the diffusibility explain certain physiologic phenomena, such as the fact that urea and NaCl are found in the cerebrospinal fluid in about the same concn. as in the blood, while only 59% of the glucose in the blood can be found in the spinal fluid. This seems to indicate that this fluid is formed by dialysis, rather than by actual secretion. Uric acid acts differently. The living membrane involved seems to display a selective action against the passage of uric acid. Dialytic diffusion is probably concerned in impregnation of the tissues, as with sugar in diabetes and uric acid in the gouty.

L. W. RIGGS

Clinical observations on certain constituents of the bile. REGINALD FITZ AND MARTHA ALDRICH. *J. Am. Med. Assoc.* 79, 2129-32(1922).—The sp. gr., viscosity, cholesterol content, total N and urea N were detd. in cases of chronic cholecystitis with and without cholelithiasis. These analyses were made on bile obtained from a known source in the biliary tract under known pathologic conditions. Bile from the gall bladder from cases of cholecystitis with gall stones tended to be less pigmented, of lower sp. gr. and less rich in N than the bile from cases of cholecystitis without stones.

Cloudy bile was often present in acutely inflamed gall bladders. Viscosity was without significance. Bile urea concn. was approx. the same as that of the blood. Unstained bile sediments in cases of acute cholecystitis usually contained numerous leucocytes. Large variations encountered in the compn. of individual specimens of bile could not be accounted for. Data from analyses could not be correlated with clinical and operative findings. Analyses of bile collected through the duodenal tube by Lyon's method would give even less trustworthy data.

L. W. RIGGS

Amino acid deficiency as the primary etiologic factor in pellagra. JOSEPH GOLDBERGER and W. F. TANNER. *J. Am. Med. Assoc.* 79, 2132-5(1922).—See C. A. 16, 3124.

L. W. RIGGS

New method of testing liver function with phenoltetrachlorophthalein. S. M. ROSENTHAL. *J. Am. Med. Assoc.* 79, 2151-4(1922); cf. C. A. 16, 3125.—Five mg. of phenoltetrachlorophthalein per kg. of body wt. is injected intravenously. This dosage is normally removed from the blood stream very rapidly. Thus in normal persons from 2 to 6% is present in the plasma 15 min. after injection, and it practically completely disappears within 40-60 min. In liver disease high percentages may be found in the plasma for many hrs. after injection. Technical details for performing the test are given. Tests upon 10 normal persons, 10 with extra-hepatic disease and 17 with various hepatic diseases show that high degrees of retention of the dye in the plasma occur in cases of liver disease. Results by this method are quant., and it is believed, that they give an index of the functional capacity of the liver.

L. W. RIGGS

Biochemical studies in diseases of the skin. II. Acne vulgaris. O. L. LEVIN and MAX KAHN. *Am. J. Med. Sci.* 164, 379-85(1922); cf. C. A. 16, 751.—In 38 patients with acne vulgaris there was no disturbance in N or Ca metabolism. There was a high blood sugar in 50% of the cases, acidosis in 30%, and an increased basal metabolism rate.

G. H. S.

Gas metabolism in anaphylactic shock. I. F. ABDERHALDEN and ERNST WERTHEIMER. *Arch. ges. Physiol.* (Pflüger's) 195, 487-98(1922).—In anaphylaxis (serum) in guinea pigs not only was the gas metabolism in the intact animal diminished but the tissue respiration was in all cases reduced. Detns. of this type may serve to correlate or differentiate the true anaphylactic reactions from the so-called anaphylactoid responses.

G. H. S.

H—PHARMACOLOGY

ALFRED N. RICHARDS

Ethereal oils and their practical use. HEINZ. *Münch. med. Wochschr.* 68, 628-31(1921).—Expts. are cited showing the increased formation of bile on administration of cholactol, which contains as active principle oil of peppermint. The use of oil of turpentine is mentioned. A method is given to make a 5% emulsion in milk for intravenous injection. Terpestrol is a powder made with lactose contg. 5% oil of turpentine. In another combination 10% urotropine is added. This is called H. T. Terpestrol.

S. AMBERG

Lausofan against head lice. H. JANKE. *Münch. med. Wochschr.* 68, 1156(1921).—Lausofan is a hexamethylene ketone, which, under addn. of the corresponding alc., cyclohexanol, is in alc. aq. soln. A single application under proper conditions removes lice and nits.

S. AMBERG

Clinical and experimental data with regard to strontium therapy. *Münch. med. Wochschr.* 68, 1344-6(1921).—Sr has a definite effect in certain diseases of the bones, and furthermore decreases the sensitiveness of peripheral nerves, having a favorable effect on pain.

S. AMBERG

The action of some gases and toxic vapors on guinea pigs and white rats. H. ZEEHUSEN. *Arch. nêrland. physiol.* 7, 146-50(1922).—The action of toxic gases, especially those used for war purposes (SO_2 , Cl_2 , COCl_2 , NO_2 , NOCl and Me_2SO_2), on animals was investigated. As compared with the extensive work done in that field, the publication offers little new information.

R. BEUTNER

The use of depilatory ointments containing sulfides and their action on the skin and hair. CL. GENOT. *J. pharm. Belg.* 4, 925-927(1922).—The prepn. most frequently employed for removing superfluous hair are ointments or lotions contg. the sulfides of Na or As, together with a certain amt. of CaO . Their value depends on the fact that NaSH and Ca(SH)_2 gelatinize keratin, thus softening the hair. Ca(OH)_2 accelerates this action. The NaSH is formed by the action of H_2O on Na_2S according to the equation $\text{Na}_2\text{S} + \text{H}_2\text{O} = \text{NaSH} + \text{NaOH}$. Ca(OH)_2 reacts with orpiment yielding Ca(SH)_2 , $\text{Ca}_3(\text{AsO}_3)_2$ and $\text{Ca}_3(\text{AsS}_3)_2$. The sulfides or the acid sulfides have no effect upon the skin, but the alkali which is formed by hydrolysis acts as a cauterizing agent. It is, therefore, necessary to remove the depilatory as soon as possible and to wash the skin thoroughly with water.

A. G. DUMÉZ

The influence of saccharin on the heart and circulation. C. VAN EWEYK. *Z. physik. diätet. Therap.* 26, 276-8(1922).—Saccharin has no demonstrable influence in doses much larger than can be given by mouth.

H. B. FINK

Therapeutic indications of ouabain. E. DESEQUELLE. *Bull. sci. pharmacol.* 29, 564-8(1922).—A review.

F. S. HAMMETT

The treatment of tuberculosis with Tebelon. C. SCHAEFER. *Deut. med. Wochschr.* 48, 1380-1(1922).—Good results are reported in the treatment of tuberculosis in children with Tebelon, the isobutyl ester of oleic acid, when the infection is localized to the skin, the lymphatics, or the bone marrow, and in cases of mild generalized infections without org. lesions. A series of case reports is submitted.

MILTON HANKE

The clinical significance of the sulfoeyanide radical. HANS FRIEDENTHAL. *Deut. med. Wochschr.* 48, 1574-5(1922).—Because of the fact that the NCS radical is therapeutically very similar to I, F. has prepd. a new deriv. of Ca, Br, and NCS that has all of the therapeutic properties of the constituent radical and can be used as a substitute for the more expensive iodides.

MILTON HANKE

The action of thallium on the endocrine system. A. BUSCHKE and BRUNO PRISER. *Klin. Wochschr.* 1, 995(1922).—Tl, when fed or injected, has a deleterious effect upon the organs of internal secretion. The apathy, somnolence, and loss of hair following such treatment can be attributed to the action of Tl on the endocrine system, especially on the sex organs. Rats fed on Tl acetate develop very slowly and as adults soon lose their sex instincts. The testicles may be completely atrophied and free from spermatozoa. The adrenals are either free from adrenaline, or contain only a fraction of the normal amt.

MILTON HANKE

The influence of various sympathetic nerve poisons on the concentration of potassium in the blood serum. K. DRESEL and R. KATZ. *Klin. Wochschr.* 1, 1601-3(1922).—The concn. of K in blood serum, detd. by the method of Kramer and Tisdall, (C. A. 15, 1912) was found to vary between the narrow limits of 22.7 to 38.8 mg. per 100 cc. The injection of 1 cc. of a 1:1000 soln. of adrenaline, a sympathetic nervous system stimulator, is followed by a rapid and marked drop in the K-ion concn. of the serum. The lowest values are obtained 30 min. after the injection. The recovery to normal is equally rapid and the K-ion concn. rises somewhat above normal for a time. The injection of 1 mg. of atropine sulfate, a parasympathetic depressor, is followed by a marked drop in the K-ion concn.; but in this case the lowest values are obtained 1 to 2 hrs. after the injection. The peroral administration of 1 to 1.5 g. of choline gives rise to a steady decline in the K-ion concn. The last detns. were carried out 3 hrs.

after the choline ingestion. The K-ion concn. was still diminishing. From this it appears that the K-ion concn. of serum is diminished whenever the sympathetic or parasympathetic nervous systems are stimulated or when the parasympathetic system is depressed.

MILTON HANKE

Bacteriological and physiologico-chemical investigations with 8-hydroxy-7-iodo-5-quinolinesulfonic acid (yatren). KURR HERZBERG. *Klin. Wochschr.* 1, 1830-3 (1922).—The early preps. of yatren were less stable than the more recent product. A product prep'd. in Sept., 1921 lost I readily when boiled for a short time in aq. soln. The more recent preps. can be heated to boiling, in aq. soln., for 15 min. without decomposing. This difference in the chem. stability of the various preps. accounts for the diverse exptl. results obtained at different times. The earth bacillus (*Erd bacillus*) is destroyed by a 24-hr. immersion in a 0.5% soln. of yatren. Anthrax succumbs after a 0.5-hr. immersion in a 0.25% soln. A bit of cambric cloth, immersed in an emulsion of bacteria and then in the yatren soln., was completely sterile in the case of staphylococci, after a 24-hr. immersion in a 5% soln., and after a 96-hr. immersion in a 2% soln. With anthrax, the cambric cloth method being used, complete sterilization was effected by a 4-hr. immersion in a 5% soln. Staphylococci are killed by a 2-min. immersion in goat serum to which 3% of yatren has been added. Immersion for 2 min. in a serum contg. 0.5% yatren inhibits the growth markedly. Yatren is more effectively bactericidal in serum than it is in water. Phenol is more effective toward staphylococci than yatren. In estg. the amt. of yatren excreted in the urine, it is best to decompose the comp'd. so that I is liberated and then est. the I. Expts. showed that FeCl_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ do not liberate I from yatren. H_2O_2 liberates I slowly and incompletely. HNO_3 gives a quant. yield of I in aq. soln.; but this reagent cannot be used in estg. the yatren concn. of urine because of excessive foaming. KMnO_4 plus H_2SO_4 is ideal for liberating I from yatren in urine. The I is extd. with CHCl_3 and its amt. estd. by titration with 0.02 N $\text{Na}_2\text{S}_2\text{O}_4$. The detailed procedure is given. When yatren is injected intravenously it is quantitatively excreted in the urine in the course of 5.5 to 6 hrs. When fed, yatren appears largely in the feces, only a small fraction appearing in the urine.

MILTON HANKE

The action of pilocarpine. O. PLATZ. *Klin. Wochschr.* 1, 2001(1922).—An injection of pilocarpine leads to an increase in the frequency of the pulse and a reduction of the blood pressure. There are no characteristic respiratory changes. The concn. of total solids and sugar in the blood is increased. The NaCl concn. is unchanged. Erythrocytes are slightly increased. Neutrophils and eosinophils are unchanged, and lymphocytes slightly increased. Increased salivation is more frequent than increased sweating. The effects of the drug are always most intense when it is introduced intravenously. The intravenous injection is tolerated quite as well as the subcutaneous injection.

MILTON HANKE

For how long and in what concentrations does salvarsan remain in human blood? H. T. SCHREUS and ALFRED HOLLANDER. *Klin. Wochschr.* 1, 2089-92(1922).—The method of Abellu was used for the detn. of salvarsan in blood serum. The serum contg. salvarsan is treated with dil. solns. of HCl and NaNO_2 . The diazotized salvarsan so obtained is coupled with resorcinol in Na_2CO_3 soln. A brilliant red color is obtained which is still discernible at a salvarsan concn. of 1:100,000. The salvarsan concn. can be quantitatively estd., approx., by covering the alk. resorcinol soln. with the diazotized salvarsan soln. and comparing the color of the intersection band with that produced by a standard soln. under identical conditions. The concn. of salvarsan in the serum drops to 1:40,000 in 15 min., 1:50,000 in 30 min., and has always reached a subdeterminable concn. within 3 hrs. The results are approx. identical regardless of the character of the salvarsan prep'n. employed.

MILTON HANKE

The pharmacology of potassium and calcium ions. MAX ROSENMAN. *Klin. Wochschr.* 1, 2093-5(1922).—Strips of intestine, urinary bladder and uterus were suspended in Ringer solns. and the tonus and rhythm of the smooth muscle fibers recorded. When K is added to a K-free Ringer soln., a drop in tonus and an inhibition of rhythm is obtained after each addn. until the physiol. K concn. is reached. Further addns. of K increase the tonus and finally produce tetanus. Increasing the K concn. beyond this point produces a reduction in tonus. Although Ca reduces the tonus when physiol. concns. of K are present, it raises the tonus when the existing concn. of K is above the physiol. The addn. of K to a K-free Ringer soln. to which pilocarpine has been previously added reduces the tonus just as it does in the absence of pilocarpine. The addn. of K, in more than physiol. concns., to a Ca-free Ringer soln. produces a reduction in tonus and injures the rhythm. When Ca is added to a Ringer soln. free from Ca or free from both Ca and K a steady increase in tonus and rhythm is obtained up to the physiol. Ca concn. Increasing the concn. of Ca produces first a reduction in tonus then an elevation, and then a reduction. If in a Ca-free Ringer soln. the tonus is reduced by means of adrenaline, addn. of Ca overcomes the effect of the adrenaline, the tonus and rhythm being increased. If a toxic dose of adrenaline is used, addn. of Ca reduces the tonus. Ergotoxin raises the tonus in a K-free Ringer soln. but reduces the tonus in a Ca-free Ringer soln.

MILTON HANKE

The basis for the use of chloramine as an antiseptic. MARIANNE GRÜNWARD AND FRANZ BASS. *Klin. Wochschr.* 1, 2278-80(1922).—Chloramine, which can be considered to be the Na salt of the mixed amide of *p*-toluenesulfonic acid and HClO, contains 12.4% of active, oxidizing Cl, and in soln. reacts chemically like free Cl. The white, odorless, cryst. solid is readily sol. in H₂O and difficultly sol. in alc. and glycerol. Injected intravenously the compd. is highly toxic; but when absorbed slowly through a mucous membrane, or through the alimentary tract it is comparatively harmless because it is rapidly converted, in the organism, into the harmless NaCl and *p*-toluenesulfonic acid amide. It is not irritating when used in concns. of 0.2 to 0.5%. Contact with living tissue does not destroy its antiseptic properties rapidly. It can be used as a mouth wash. Cotton and linen are not attacked by chloramine, but wool and silk are attacked. The taste of the prepn. can be improved by the addn. of menthol, but oil of gaultheria must not be used. Glycerol, starch, vaseline. gum, and stearic acid may be used as saline vehicles.

MILTON HANKE

A report following the use of mercurous in the treatment of one hundred and fifty cases of syphilis. W. E. KEANE AND J. C. SLAUGENHAUPT. *J. Urol.* 8, 197-208 (1922).—Mercurous is a white powder, freely sol. in H₂O giving a slightly alk. soln. which is permanent provided it be protected from the light. It is derived from Hg acetate and acetylsalicylic acid. By wt. it contains about 44% metallic Hg. The phenol coeff. of mercurous against *B. typhosus* is approx. 2. The coeff. of HgCl₂ under the same conditions is about 1000. Its use in 150 cases of syphilis is reported. The av. dose is 0.1 g. and is given intravenously. While mercurous gives no better or quicker results than other mercurials in the treatment of syphilis it has the advantage of a low toxicity.

JULIAN H. LEWIS

The effect of carbon dioxide on respiration after poisoning by carbon monoxide. J. MELLANBY. *Proc. Physiol. Soc., J. Physiol.* 56, xxxi(1922).—After the respiratory movements of an animal have been diminished or annulled by CO a marked stimulation of breathing can be produced by CO₂. The administration of O₂ has no such effect, but O₂ during the hyperpnea produced by CO₂ results in the rapid elimination of CO from the animal's body.

J. F. LYMAN

The heat production and the mechanism of veratrine contraction. W. HARTREE AND A. V. HILL. *J. Physiol.* 56, 294-300(1922).—A study of heat liberation in vera-

trized skeletal muscle shows that the prolonged veratrine contraction cannot be ascribed to a slowing of relaxation, or of the chem. processes by which the acid that excites the mech. response is removed from the site of its activity. The effect of veratrine seems to be on the mechanism which in the normal muscle cuts short and controls the liberation of energy following a single shock.

J. F. LYMAN

The influence of drugs on the precipitation rate of blood corpuscles. N. ISHWARI. *Intern. Med. News* (Japan) No. 998(1921); *Japan Med. World* 2, 77.—In the rabbit, adrenaline, peptone, $\text{Ba}(\text{ClO}_3)_2$, NaHCO_3 , and NaCl accelerate pptn., and digifolin and atropine also to a slight degree. Chloral hydrate, urethan, and cinomene-HCl, retard the pptn. when injected intravenously. When tested *in vitro*, adrenaline accelerates the pptn., but chloral hydrate, urethan, and cinomene-HCl retard the action remarkably, while atropine and peptone have no influence on the pptn.

M. E. MAYER

The treatment of sleeping sickness with "Bayer 205" and the behavior of the drug in the human body. MARTIN MAYER AND W. MENK. *Arch. Schiffs-Tropen Hyg.* 26, 208-12(1922); cf. *C. A.* 16, 3128-9.—In a case of sleeping sickness resistant to As and Sb treatment the trypanosomes disappeared rapidly from the blood on intravenous treatment with "Bayer 205". The drug was present in an active trypanosomocidal form in the urine 12 days after the last injection and in the blood 13 days. In oral administration of the drug albuminuria occurred shortly afterwards, greater in intensity but more transient than the albuminuria following intravenous treatment. The serum showed a weak trypanosomocidal reactivity 8 days after oral administration.

W. A. PERLZWEIG

The absorption and activity of the trypanosomocide "Bayer 205" in intravenous treatment. MARTIN MAYER. *Arch. Schiffs-Tropen Hyg.* 26, 237-43(1922); cf. preceding abstr.—Goats infected with *Trypanosoma rhodesiense* were cured by oral administration of "Bayer 205." By means of prophylactic feeding of the drug a goat and a dog were protected against large infecting doses of trypanosomes. The serum of the goats after several weeks of treatment with the drug showed trypanosomocidal effects when injected into infected mice. The milk of the same goats when fed to normal mice protected the latter against subsequent infection. Larger doses of the drug were required for treatment and prophylaxis when administered by mouth than in subcutaneous and intravenous administration.

W. A. PERLZWEIG

Therapy in Leishmania cutanea. W. A. POSPELOV. *Arch. Schiffs-Tropen Hyg.* 26, 202-5(1922).—Successful treatment with local application of CO_2 snow is described.

W. A. P.

Treatment of "mal de caderas" of horses with the new drug "Bayer 205." L. E. MIGONE AND T. OSUNA. *Arch. Schiffs-Tropen Hyg.* 26, 289-304(1922).—"Mal de caderas" is an infectious epidemic disease of horses caused by *Trypanosoma equinum* and is prevalent in South America. M. and O. found that 2-4 g. of "Bayer 205" injected intravenously at 8-day intervals invariably cured infected horses. They also used the drug prophylactically with success.

W. A. PERLZWEIG

A study of metabolism in chloroform poisoning. F. P. UNDERHILL AND ROBERT KAPSIHOW. *J. Metabolic Research* 2, 57-72(1922).—Graham's hypothesis (*C. A.* 9, 2109) that in late poisoning with CHCl_3 and with other alkyl halides the intoxication is due chiefly to the liberated HCl was not confirmed. A diet yielding an alk. ash when fed to rabbits had no inhibiting effect upon delayed CHCl_3 poisoning. The Cl excretion in CHCl_3 -poisoned rabbits was not increased in starvation. The only metabolic changes observed with the alk. diet, that could not be explained by the food, were alterations in the creatinine, creatine and total N excretion. These are probably the results of absorption of dead tissue following CHCl_3 injury.

W. A. PERLZWEIG

The influence of benzyl benzoate upon nitrogenous metabolism. G. T. PACK AND

F. P. UNDERHILL. *J. Metabolic Research* 2, 73-105(1922).—Judging from exptl. investigations on dogs, the therapeutic dose of benzyl benzoate for human beings is probably insufficient to disturb the normal nitrogenous metabolism. Larger doses, *i. e.*, above 0.5 cc. per kg. of body wt., bring about an increase of protein katabolism in dogs. The titratable acidity and total PO_4 excretion in the urine are augmented. The total N output is increased. A marked creatinuria occurs. Conjugated glucuronates appear in the urine. Creatinine metabolism is unmodified. The changes that occur are probably brought about by BzOH , either when introduced as benzoates or by conversion from the $\text{C}_6\text{H}_5\text{CH}_2$ grouping. Benzyl succinate produces less change in the normal nitrogenous metabolism of the dog than the other C_6H_5 derivs. investigated. A new ester, dibenzyl succinate, is suggested for pharmacol. investigation. Several theories are submitted relative to the katabolic processes that ensue following the administration of these C_6H_5 derivs. W. A. PERLZWEIG

The influence on metabolism of some purine and pyrimidine bases. F. P. UNDERHILL AND H. F. FARRELL. *J. Metabolic Research* 2, 107-11(1922).—Solus. of caffeine, theobromine, uric acid, and of hypoxanthine when injected into fasting rabbits led to an augmented excretion of total N, creatine and creatinine, indicating an increased protein katabolism. Uracll gave discordant results in 2 rabbits. W. A. PERLZWEIG

Intravenous experiments with eserine in the examination of the vegetative system; the amphotropism of this substance. D. DANIELOPOLU AND A. CARNIOL. *Presse med.* 30, 685-6(1922).—When injected into sympathicotonic patients eserine in 1-mg. doses has a more rapid and marked effect on the sympathetic system and a more retarded and less marked vagus effect than observed in normal subjects under the same dose. In vagotonic subjects the same dose has no sympathetic effect and does not elevate the blood pressure as it does in normal subjects. A certain group of subjects are designated as amphotonic; in these both the sympathetic and vagus effects were pronounced. W. A. PERLZWEIG

Treatment of epilepsy by intravenous injections of arsphenamine. M. PAGE. *Presse med.* 30, 777(1922).—Encouraging results in 3 cases are described. W. A. P.

Quinidine and digitalis therapy. L. CHENISSE. *Presse med.* 30, 734-5(1922).—Review. W. A. P.

Treatment of chorea by intraspinal injections of magnesium sulfate. D. E. PAULIAN AND R. DRAGESCO. *Presse med.* 30, 680-1(1922). W. A. P.

The action of tissue diuretics. HANS MOLITOR AND E. P. PICK. *Wiener klin. Wochschr.* 35, 389-91(1922).—Frogs are shown to be superior to mammals in the study of diuretics, because of the rapidity of change of temp. and the consequent easily observed rapid changes in the water content of the tissues. These changes according to M. and P. are due to colloidal swelling and hysteresis. "Novasurol," HgCl and urica produced distinct diuretic effects while caffeine did not. W. A. PERLZWEIG

The treatment of gonorrheal infection of the scrotum with intravenous injections of calcium chloride. E. RADNAL. *Wiener klin. Wochschr.* 35, 902-3(1922). W. A. P.

The treatment of syphilis with trepol. R. RÖSNER. *Wiener klin. Wochschr.* 35, 919-21(1922).—Trepol is a com. prepn. described as a compd. of tartrates and bis-muthates of Na and K. It is being widely experimented with in the treatment of syphilis in France, chiefly by Levaditti and his associates (cf. *C. A.* 16, 3702-3). R. finds that the drug has a rapid effect upon the disappearance of clinical symptoms and of spirochetes from the blood. The Wassermann reaction, however, persists for a somewhat prolonged period. W. A. PERLZWEIG

Tetrachloroethane poisoning. N. FIESSINGER AND M. WOLF. *Annales de Médecine* (Paris) 12, 269(1922); *J. Am. Med. Assoc.* 79, 2119.— $\text{C}_2\text{H}_2\text{Cl}_4$ used in the manuf. of artificial pearls, appeared responsible for 2 cases of toxic jaundice. The first symptoms

were fatigue, nausea, headache, constipation and sometimes vomiting. The jaundice did not appear till the 3rd or 4th day. The necropsy findings in a fatal case and the results of expts. with white mice show the highly toxic nature of C_3H_7Cl , and that the liver suffers first. In France the use of this chemical has been abandoned in making airplanes. Alk. treatment with Na citrate and carbonate, supplemented with an abundance of sweetened beverages, is recommended.

L. W. RIGGS

Delirium in uremia provoked by calcium. P. PAGNIEZ AND A. RAVINA. *Bull. soc. med. hopitaux* 46, 1451(1922); *J. Am. Med. Assoc.* 79, 2255.—The case in question was a nephritic having an azotemia of less than 0.1%, with hypertension, albuminuria, permanent edema, and constant gallop rhythm. The administration of 8 g. of $CaCl_2$ produced a violent reaction, delirium and attempted suicide. The effect is ascribed to the large dose of a crystalloid and not to any special action of Ca. Action of calcium chloride in normal persons. A. LEMIERRE AND J. LEVESQUE. *Ibid* 1453 and 2255, resp.—A healthy man on a salt-free diet received daily 12 to 8 g. of $CaCl_2$. The subject lost wt. and was extremely depressed mentally and physically. Stopping the $CaCl_2$ and taking NaCl produced a state of exhilaration, a gain in water and for 48 hrs. the subject was "salt drunk." The threshold of chloride was lowered while it did not change in a case of nephritis in which the urosecretory index was made worse. The expt. again shows the potent action of $CaCl_2$ on the interstitial circulation and the hydration of the organism.

L. W. RIGGS

Lethal agent in acute intestinal obstruction. R. W. GERAED. *J. Am. Med. Assoc.* 79, 1551-4(1922); cf. *C. A.* 16, 2364.—Death in acute ileus results from a systemic poisoning by histamine and other putrefactive products formed in the lumen of the obstructed bowel by bacteria and passed through the mucosa (seemingly into both blood and lymph) when the mucosa has become asphyxiated and lost its vital powers of selection, subsequent to distention and interference with its normal circulation.

L. W. RIGGS

Effect of sodium citrate on the blood, especially the p_H factor. R. R. MELLON, W. S. HASTINGS AND G. U. CASEY. *J. Am. Med. Assoc.* 79, 1679-81(1922).—An attempt to show the formation of anticomplementary substances from the action of Na citrate on both whole blood and washed corpuscles failed except when so large an amt. was employed that sufficient citrate was present to have this effect in itself. The anticomplementary action of citrate seems to be independent of the H-ion concn. of the soln. used. No increase in the fragility of red cells was observed from any citrate soln. employed, nor was there any decrease in the phagocytic index of leucocytes. It is not concluded that Na citrate is entirely harmless or without effect on the blood used in transfusion but that it is without effect on the immune reactions studied. It appears that moderately acid or alk. solns. are quickly neutralized after injection into the blood stream. Accordingly if the p_H factor is of importance its action more probably is associated with the disturbances of colloidal equil. which may accompany the rapid neutralization of solns. with an abnormal p_H value.

L. W. RIGGS

Hexamethylenetetramine as a diuretic. H. O. RUH AND P. J. HANZLIK. *J. Am. Med. Assoc.* 79, 1980-2(1922).—The influence of $(CH_2)_6N_4$ in 1 g. and in 5.2 g. doses on the urine output was studied in 3 subjects (convalescent boys) under controlled conditions. The results of 5 expts. show conclusively that the drug is not a diuretic. The duration of excretion of the drug in urine ranged from 20 to 41 hrs., being somewhat longer with the larger doses used, but independent of the fluid intake and diuresis. This is contrary to current conceptions. The total excretion was variable and ranged from 32 to 82%, which was also independent of dosage, fluid intake and diuresis.

L. W. RIGGS

Carbon tetrachloride in the treatment of hookworm disease. S. M. LAMBERT.

J. Am. Med. Assoc. 79, 2055-7(1922).—Expts. and observations in 20,000 cases led to the conclusions that CCl_4 is a vermifuge and a vermicide of great potency. It gives little discomfort to the patient. It permits treating rapidly, at a low cost, vast populations suffering from hookworm disease. One treatment to each individual in a given area lowered the infection rate from 100% to less than 9.

L. W. RIGGS

Pharmacology of mercury. Wm. SALANT. *J. Am. Med. Assoc.* 79, 2071-4(1922).—Expts. with frogs, turtles, dogs, cats and rabbits showed that Hg is highly toxic to the heart, causing disturbances such as heart block, delirium cordis and finally paralysis. It is also toxic to the respiration to a less pronounced degree. The action of Hg salts may be greatly increased by the previous injection of citrate or of adrenaline.

L. W. RIGGS

Some new hypnotics of the barbituric acid series. H. A. SHONLE AND A. MOMENT. *J. Am. Chem. Soc.* 45, 243-9(1923).—A no. of 5,5-dialkyl- and 5-alkyl-5-arylbarbituric acids were tested for hypnotic action. The monoalkyl and monoaryl derivs. injected subcutaneously in rabbits are inactive in doses of 0.5-1.0 g./kg. body wt. The di-Me compd. has no apparent action in 0.75 g. dose; as the mol. wt. increases the activity increases to a max. and then decreases until the hypnotic activity is lost and the animal shows only muscular incoordination or no effect at all. However, the length and type of the substituent C chains play an important part; branched chains are more active and less toxic than straight chains. Below are given, resp., the dose (in g./kg. body wt.) which makes a rabbit unable to rise when shaken and the toxic dose of various barbituric acid derivs.: Et, —, — (0.5 g., slight symptoms); PhCH_3 , —, — (0.5 g., no action); Bu, —, — (1.0 g., no action); Me₂, —, — (0.75 g., no action); Et₂, 0.15, 0.25; Pr, 0.06, 0.22; $\text{Pr}(\text{Me}_2\text{CH})$, 0.05, 0.15; Bu₂, 0.35, 0.50; $(\text{PhCH}_2)_2$, —, — (0.5 g. ineffective); $(\text{Me}_2\text{CH})\text{Et}$, 0.10, 0.20; (iso-Bu)Et, 0.05, 0.12; BuEt, 0.04, 0.10; (sec-Bu)Et, 0.05+, 0.20—; (iso-Am)Et, 0.04, 0.17; (iso-Am)Pr, 0.08, 0.22; $(\text{PhCH}_2)\text{Et}$, 0.04, 0.06; $\text{PhCH}_2(\text{Me}_2\text{CH})$, 0.20, 0.35; $(\text{PhCH}_2)\text{Pr}$, 0.20, 0.45; PhEt , 0.08, 0.15. In dogs 0.017-0.025 g. of the isoamylethyl compd. per kg. body wt. produced a deeper sleep than 0.035-0.074 g. barbital and 0.025 g. luminal had no apparent hypnotic action. Contrary to expectation from Macht's work on the antispasmodic or relaxant action of PhCH_2OH , benzylethylbarbituric acid, while a more active hypnotic than barbital, causes tetanic convulsions in dogs. Below are the h. ps. (pressure in parentheses), d_{25}^{25} and n_D^{25} of the diethyl disubstituted malonates prepd. for the synthesis of the barbituric acids: sec-butylethyl, 155-60° (60), 0.9858, 1.4264; butylethyl, 125-30° (12), 0.9756, 1.4222; isobutylethyl, 119-20° (8), 0.9682, 1.4228; isoamylethyl, 150° (20), 0.9540, 1.4255; propylisopropyl, 143° (42), 0.9803, 1.4239; butylisopropyl, 136° (14), 0.9742, 1.4291; isoamylisopropyl, 140° (25), 0.9575, 1.4273. M. ps. of the substituted-barbituric acids: butyl 210-5°, isobutylethyl 174-6°, isoamylethyl 154-6°, butylethyl 126-8°, butylisopropyl 209-10°, propylisopropyl 161-2°, isoamylisopropyl 173-5°, isoamylpropyl 129-32°, sec-butylethyl 155-7°.

C. A. R.

Mydriatics and miotics: The relation between chemical structure and physiological activity. M. TIRRENEAU. *Rev. gen. sci.* 33, 544-52, 583-92(1922).—A review.

GEORGE ERIC SIMPSON

The action of drugs on respiration. I. The morphine series. C. F. SCHMIDT AND W. B. HARER. *J. Exptl. Med.* 37, 47-65(1923).—Morphine and heroine were found to exert a selective depressant action on the central expiratory mechanism and the slower rate, with relatively unaltered depth, seemed to be due at least partly to the slower rate of emptying the lungs. Codeine had no depressant action on the respiration of decerebrated cats. Larger doses of morphine or heroine had no further depressant effect on rate or depth of breathing after expiration was made passive, unless circulatory depression appeared. In decerebrated animals large doses of morphine

and moderate doses of codeine stimulated the spinal cord and expiration became active with a faster rate of breathing. The characteristic action of morphine and heroine on the respiration of the cat is apparently limited to a depression of active expiration.

II. Ether, chloroform, chloral, urethan, luminal, magnesium, caffeine, strychnine and atropine. *Ibid* 69-81.—The depressant drugs which have been studied were found to resemble morpline and heroine in that they depressed expiration more than inspiration, but they acted only in narcotic doses and always depressed inspiration at the same time. The sp. action of each drug is given. Mg seemed to produce the most uniform, uncomplicated depression of all the depressants tried. Luminal resembled morphine and heroine more closely than any of the general depressants. C. J. WEST

I—ZOOLOGY

R. A. GORTNER

Origin and function of chromatophores (pigment cells) in the liver of the selachians. J. C. HEMMETER. *Arch. nêrland. physiol.* 7, 165-73 (1922).—Concerning the origin and the chem. compn. of the chromogen substance that gives rise to pigment cells in the liver of certain fish, H. states that it must be formed from the food because no chromatophores are found in the liver of a young selachian or mustelus, born in the aquarium and having been kept without food. H. suggests that it might have been formed from amino acids by tyrosinase in the way described by Chodat (*Abderhalden's Handbuch Biochem. Arbeitsmethoden*, III, 62) and that it plays a role in temp. regulation and as a N reservoir for the urea present in a high concn. (2.6%) in the blood of the fish. R. B.

Iodine and anuran metamorphosis. W. W. SWINGLE. *Science* 56, 720-1 (1922).—Thyroidectomized and hypophysectomized tadpoles of *R. sylvatica* metamorphosed in the normal manner though less slowly when fed 3,5-diiodotyrosine, while the 3,5-dibromo compd. or pure tyrosine was ineffective. 3,5-Diiodotyrosine is more effective than inorg. I; both of these are useless in case of mammals. B. S. N.

Irritation and irritability. F. MARCHAND. *Arch. Entwickl. Organ.* 51, 256-83 (1922).—Review. CHAS. H. RICHARDSON

12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

The place of the laboratory man in the world of food economies. E. V. MCCOLLUM. *Am. Food J.* 17, No. 12, 17-8 (1922). H. A. LEPPER

Food flavors: their source, composition and adulteration. J. W. SALE AND W. W. SKINNER. *Am. Food J.* 17, No. 5, 13-5, No. 6, 31-2, No. 7, 27-9, No. 8, 27-8, No. 9, 29-30, No. 12, 29-31 (1922).—A discussion of 89 various products used as food flavors, with a bibliography of 78 references. H. A. LEPPER

The margarine industry of France. A. GUILLAUME. *Bull. sci. pharmacol.* 29, 578-87 (1922).—A review. F. S. HAMMETT

The water content of margarine. A. GRONOVER AND FR. BOLM. *Chem. Ztg.* 46, 933-4 (1922).—The H₂O content of margarine in tubs (25-130 lbs. capacity) is uniformly distributed. In pound prints it is not uniform. The claim of the industry that the pressing of margarine into cubic form eliminates H₂O is shown not to be the case. H. A. LEPPER

Analysis of butter and margarine. M. MONHAUPT. *Chem. Ztg.* 46, 831 (1922).—Simple methods for detn. of fat, H₂O, NaCl and "non-fat" are given. H. A. LEPPER

Cultivation of the olive and manufacture of olive oil. J. BONNET. *Bull. mal.*

grasses 1922, No. 5, 95-126.—A general report covering cultivation, exploitation and treatment of diseases of the olive, the manuf. of the oil, care of the olive and treatment of mill residues.

Food poisoning and its prevention. CHAS. THOM. *Am. Food J.* 17, No. 11, 15-16, 33-36(1922).—A discussion of food poisoning, chiefly *botulism*, and its control by law-enforcement officials.

E. SCHERUBEL

H. A. LEPPER

Comparative milling and baking qualities of kanred, black hull and turkey red varieties, Oklahoma wheat. H. F. VAUPEL. *J. Am. Assoc. Cereal Chem.* 7, 167-73 (1922).—The av. milling yield for kanred and turkey red were about the same, while that of black hull was the highest. Av. test wt. for kanred was 58.8 lb.; black hull 61.0; and turkey red 58.8 lbs. The av. protein content for kanred samples was 11.31%, black hull 10.67% and turkey red 11.56%. Purer strains of turkey red averaged about 12 to 12.5 while black hull for a dark red wheat averages between 10.5 to 11.00. Av. absorption of kanred samples was 63.1%, black hull 58.3% and turkey red 63.5%. Av. loaf vol. of kanred samples was 2275 cc., black hull 1995 cc. and turkey red 2405 cc. The flour of black hull variety resembles flour of soft wheat varieties in absorption and loaf volumes. Flour of black hull variety lacks strength. In baking vol. turkey red seems to be superior. Some of the individual kanred samples were equal to turkey red.

RUTH BUCHANAN

Diastatic enzymes of wheat flour and their relation to flour strength. L. A. RUMSEY. *Am. Inst. Baking Bull.* 8, 85 pp.(1922).—Diastatic enzymes are recognized as one of the important factors which go to make up flour strength. Expts. to define more clearly the action of diastase in the production of better bread are indicated by a review of the literature dealing with the different factors of flour strength. The effects of diastatic enzymes of the wheat flour in panary fermentation, with respect to concn., time, temp., acidity, and diastatic power, have been detd. The baking values of 14 representative flour samples were detd. by comparative baking tests. Other valuable analytical data are tabulated along with these baking values in order to correlate as many different factors as possible with the strength of each flour. Protein pptn. from cereal exts. by the tungstic acid reagent of Folin and Wu was studied in its application to the detn. of diastatic power in flour. Max. activity of flour diastase in a dough at any given temp. or pH is not reached at once because of insufficient water. Optimum H-ion concn. for flour diastase is seldom reached during the fermentation of a normal dough. Temp. is the most important factor in the control of diastatic action in the dough. The flour showing the greater diastatic power should show the greater strength and consequently the greater baking value, providing the relative quality and quantity of the gluten are the same.

RUTH BUCHANAN

Ash on flour. J. R. HESS. *J. Am. Assoc. Cereal Chem.* 7, 213-7(1922).—Errors in manipulation in the detn. of ash are discussed.

RUTH BUCHANAN

Lead in self-raising flour. N. T. FOX. *Analyst* 47, 468-9(1922).—B. P. limits the Pb in $KHC_4H_4O_6$ to 20 parts per million; yet $CaH_2(PO_4)_2$ or $KHC_4H_4O_6$ substitute has no legal recognized limit for Pb. Recent tests have shown that the substance contains 200-2000 parts per million of Pb; it can be made as free from lead as CaH_2O_6 . $CaH_2(PO_4)_2$ can be made with less than 10 parts per million of Pb and is sold with this guarantee.

RUTH BUCHANAN

Determination of chlorine in bleached and natural flour. O. S. RASK. *J. Assoc. Official Agr. Chem.* 6, 68-71(1922).—The results of a collaborative study of the detn. of Cl in flour by 2 different methods are given. The materials used consisted of unbleached and chlorine-bleached portions of a hard-wheat patent flour milled in a commercial mill under the writer's supervision.

RUTH BUCHANAN

Determination of the volume of bread. ARPIN AND (MISS) T. PÉCAUD. *Ann.*

fuls. 15, 394-8(1922).—Carefully fill the cavities, fissures, etc. with 60 g. of clay, apply with a brush a coat of a soln. of rubber in benzine, let dry, spray on a thin coat of cellulose acetate (in AmOAc), dry by means of compressed air, insert an iron rod provided with a handle (applying clay where the rod enters the bread), and carefully lower into a vessel of water filled to overflowing. Collect the overflow in a graduate. The rate of immersion should be as rapid as possible and depends on the rate of overflow (generally 25-30 sec.). As soon as the overflow stops, withdraw, wipe, and reweigh the bread to find the amt. of absorbed water (usually 5-10 g.); add this to the amt. of overflow. As the varnish is very thin, the operation can be repeated but once. Duplicates carried out the same day showed differences of 3-19 g. per kg. of bread. The method is useful for comparing breads from different flours, but baked together. A. P.-C.

Estimation of starch in barley and wheat. A. J. LING. *Chem. News* 125, 346-7; *Chem. Age* (London) 7, 790-1(1922).—Ground barley or wheat is extd. for 3 hrs. with alc. of d. 0.920 to remove some of the proteins. It is then converted into a paste with hot water and treated with the ext. of a malt of known diastatic power for an hr. The maltose is estd. and the starch calcd. by the formula: $S = 94.73M'/M$, in which S is the percentage of starch in the sample, M is the percentage of apparent maltose produced from dry barley or wheat starch by the action of malt ext. from malt of a definite diastatic power, and M' is the percentage of apparent maltose produced from the sample and with malt of the same diastatic power. The values 63.9 and 64.0 were obtained as the percentage of starch in wheat.

RUTH BUCHANAN

Chemical test for heat damage in wheat. W. L. FRANK. *J. Am. Assoc. Cereal Chem.* 7, 218(1922).—The test consists in making a tiny "dough" out of 1-2 mg. flour on a glass slide by the addition of a drop of eosin soln. (0.2 g. H₂O-sol. eosin in 1000 cc. H₂O) and gently rubbing or mixing the flour and liquid with a second piece of glass. Note the formation of carmine-colored "gluten rools" due to absorption of the eosin by the gluten if the kernel is sound, and the specked appearance of the "mealy" dough (devoid of gluten rools) when made from a heat-damaged kernel. RUTH BUCHANAN

Crude-fiber detns. S. J. LAWELLIN. *J. Am. Assoc. Cereal Chemists* 7, 208-13 (1922).—A comparison is made of the single-and-double filtration methods of detg. crude fiber both with and without the removal of the fat and also the single-filtration method as modified by the Am. Assoc. Cereal Chemists. The methods were tried out on 14 samples so chosen as to cover nearly all crude-fiber analyses met with in an industrial cereal lab. A table gives results. The single-filtration method as modified by the Am. Assoc. Cereal Chemists, is fully as reliable as the method of the Assoc. of Official Agr. Chemists. Weigh 2 g. finely reduced material, ext. 16 hrs. with Et₂O in a Soxhlet app. Transfer fat-free material to a 1. flask (Erlenmeyer), boil exactly 30 minutes with 200 cc. 1.25% H₂SO₄, then without filtering add 200 cc. 3.52% NaOH and boil exactly 30 min. Remove the sample from the fire, add excess of concd. HCl (d. 1.18) by pouring cautiously down the sides of the flask. Excess of acid is indicated by change of color and breaking up of colloids. Filter through an aluminum crucible of max. porosity, wash with water until free from acid, then with alc. and Et₂O. Dry, weigh, incinerate, and weigh again.

RUTH BUCHANAN

Types of crude fiber. A new method for the determination and identification of flour in foods. A. FORNET. *Chem.-Ztg.* 46, 969-70; *Z. ges. Getreidev.* 14, 58-61(1922).—The amt. of flour in food is estd. by prepn. of its crude fiber and microscopical comparison with crude fiber from a known amt. of the same kind of flour; the kind of flour is detd. by comparison of color of crude fiber with that from known sources.

HARRY J. DEVEL, JR.

Points of interest respecting preserved food, more particularly that supplied to the fleet. T. J. UNDERHILL. *J. State Med.* 30, 336-55(1922).—A history of the preserva-

tion of food is given. During recent years the action of different food products on Sn has been overcome by treating Sn plates with a specially prepd. lacquer consisting mainly of shellac and sandarac and baking the treated sheets. No coating will stand sterilization at a high temp. of meat products, broths, etc. No preservatives should be allowed. Contamination from other causes such as small drops of solder and foreign flavors such as used in lacquering the outside of tins or rancid oils used in the manuf. of stamped tins is to be avoided. The processes of packing canned beef, mutton and boiled beef are discussed in detail.

RUTH BUCHANAN

Changes in oil used in frying sardines. H. R. BEARO. *Calif. Fish and Game Comm. Circ.* No. 1, 8 pp.—Conclusions: (1) The use of corn oil and a hydrogenated oil (Crisco), in addn. to cottonseed oil, is feasible. (2) The presence of varying quantities of fish oil, and the action of air and heat are largely responsible for the changes which take place in fry-bath oil. (3) Sardine oil is present to a greater or less extent in fry-bath oil used for frying sardines. When fat sardines are fried its increase is so rapid that it is not long before the fish are being fried in an oil which is largely sardine oil. To keep the sardine oil content of the fry-bath low, the sardines should be fried in the min. quantity of oil. This covers all cases except where the oil content of the bath is increasing as it does when very fat sardines are fried. Then the oil should be allowed to increase, as far as conditions will permit, as long as a condition exists. (4) Attempts to reclaim used fry-bath oil by chem. treatment have been unsuccessful. It is not probable that a cheap, successful method will be developed.

RUTH BUCHANAN

Guava (*Psidium guava*, L.). A. AZADIAN. *Ann. fals.* 15, 405-8(1922).—A 200-g. sample of fruit was boiled repeatedly with water and filtered through muslin. The cold soln. was made up to 1,000 cc., filtered through paper, and on analysis gave the following results: ext. (1) with pumice stone 8.23, (2) without pumice 8.30, (3) by refractometer 8.10, ash 0.84, direct polarization +0.5°, invert polarization -1.3°, invert sugar 3.65%, total sugars 8.25%. The analysis of the seeds gave: H₂O 10.30, N 2.44, crude proteins 15.25, total ash 3.00, ash sol. in HCl 2.69, alky. of ash (as K₂O) 0.40, tannin 1.38, glucose 0.10, fat 14.30, crude fiber 42.40, starch 13.25%. The oil was extd. from the crushed seed with a mixt. of CHCl₃, Et₂O and petr. ether, freed from solvent by distn. and subsequent heating on the water bath, filtered, and analyzed, giving the following max., min., and av. values for 5 samples: d_{40}^{20} 0.9243, 0.9306, 0.9124; refractometer (Zeiss) reading at 40° 66.4, 50.7, 57.4; n_{40}^{20} (Abbé) 1.4700, 1.4587, 1.4632; I no. 134.5, 127.9, 131.1; sapon. no. 216.0, 190.0, 197.1; acid no. 0.70, 0.34, 0.55; sol. volatile acids 0.38, 0.20, 0.26; insol. volatile acids 0.30, 0.20, 0.25; essential oil 0.03, 0.25, 0.27%. Halphen and furfural reactions were both negative in every case. Freshly cut leaves averaged 67% moisture. The dry leaves gave: Et₂O ext. 5.90, tannin 8.75, ash 11.0, water-sol. ash 4.63, ash insol. in HCl 1.36, Cl 1.10, alky. of ash (as K₂O) 18.10, crude fiber 15.75%.

A. P.-C.

Coffee from Uganda, the Sudan and Ceylon. ANON. *Bull. Imp. Inst.* 20, 294-300(1922).—The article is concerned mainly with the yields, and com. value of various varieties. The following analyses are given of coffee beans from Ceylon:

	Robusta.	Hybrid.	Canephora.	Quillou.	Uganda.
Moisture	10.1	10.1	10.4	10.4	10.6
Caffeine	2.1	2.3	2.3	2.4	2.3
Crude proteins	13.4	11.5	11.4	11.2	12.4
Fat	6.7	6.1	7.8	6.9	7.1
Carbohydrates (by diff.)	49.6	52.1	49.3	51.5	50.8
Crude fiber	14.6	14.5	15.3	14.1	13.5
Ash	3.5	3.4	3.5	3.5	3.3

A. P.-C.

Analytical data on mead. DEMOLEN. *Ann. fals.* 15, 389-94(1922).—Analyses of 18 samples of known origin are given and commented on. In order to detect adulteration the following detns. should be made: fixed acidity, sol. ash, alky. of sol. ash, non-sugar ext., rotation after complete fermentation (giving quant. detn. of the residual sugars), Fiehe reaction (for artificial invert sugar).
A. P.-C.

Determinations of acids in silage. W. ZIEGLSTORFF AND F. BENIRSCHKE. *Chem.-Ztg.* 46, 939(1922).—Interfering color in titration of total acid is removed by heating with kieselguhr several min. by refluxing before filtration and titration using phenolphthalein. Alkali blue or thymolphthalein cannot be used. Steam distn. for free volatile acids should be continued until a test drop is acid-free to Congo red. In some cases in detg. combined volatile acids, acidity continued for 800-900 cc. of distillate. In such cases the test is discontinued and max. value taken.
H. A. LEPPER

Factors influencing quality and composition of sunflower silage. M. J. BLISH. Montana Agr. Expt. Sta., *Bull.* 141, 22 pp.(1921).—There is a much greater loss of food constituents in silage made from sunflower plants cut at an early stage of growth than in silage from plants that are practically mature. The sol. sugars of the sunflower plant are chiefly fructose and sucrose, fructose predominating. They disappear during the curing process. The acidity and alc. content decrease as the stage of maturity advances. Silage made from plants in early stages of maturity is likely to be more acid, darker in color, and of slightly inferior quality to that made from plants in the later stages. Surprisingly large quantities of mannitol (as much as 9%), which is produced by fermentation of fructose, were found in many of the silage samples. Some samples of good quality contained little or none; it probably has no bearing on the matter of quality and palatability of the silage. Mannitol has a high calorific value, and since it is probably readily oxidized in the animal organism its value as an energy producer may be in some cases considerable.
J. J. SKINNER

A chemical study of broom corn and broom-corn silage. C. T. DOWELL AND W. G. FRIEDEMANN. Oklahoma Agr. Exptl. Sta., *Bull.* 135, 7 pp.(1922).—The compn. of stover from broom corn with second head, and the compn. of the silage made from the green plant are given. Broom corn cut when it was beginning to head contained 0.0098% HCN. The plant contained 0.2% and the seed 0.58% tannin.
J. J. SKINNER

The protein requirements of dairy cows. J. L. HILLS, J. L. BRACH, A. A. BORLAND, R. M. WASHBURN, G. F. E. STORY AND C. H. JONES. Vermont Agr. Expt. Sta. *Bull.* 225, 199 pp.(1922).—Many analytical data are given showing the relation of the digestible nutrients consumed to the yield and compn. of the milk.
J. J. SKINNER

The nutritive value of cattle feeds. III. Dried apple pomace for farm stock. J. B. LINDSEY, C. R. BEAK AND J. G. ARCHBOLD. Massachusetts Agr. Expt. Sta., *Bull.* 205, 135-144(1921); cf. *C. A.* 16, 299.—Kiln-dried apple pomace is a strictly carbohydrate feed with a high sugar content and lacking in true starch. It is high in fiber, but low in both protein and total ash; P_2O_5 and K make up fully 40% of the ash. It is fairly well digested by sheep, especially with respect to total dry matter, fiber and extract matter. Protein and fat are rather poorly digested. As a substitute it is but slightly inferior to both dried beet pulp and corn meal when fed to dairy cows as a component of the daily ration. It is of doubtful value for pigs, as a food for horses it is not recommended.
J. J. SKINNER

Etiwatakala grass as a fodder. ANON. *Bull. Imp. Inst.* 20, 300-2(1922).—Grass from the Portuguese Congo (probably a mixt. of *Melinis minutiflora* and *M. effusa*) gave the following results on analysis: H_2O 7.7, crude proteins 5.7, oil 1.9, fiber 33.6, carbohydrates (by diff.) 43.8 (including 1.1% of reducing sugars calcd. as dextrose), ash 7.3%. It is of fair quality as a fodder.
A. P.-C.

Toxicity of the seeds of *Jatropha mahafalensis*, Jum. (Betrata). ANON. *Bull. agence gen. colonies* 15, 190(1922); *Bull. Imp. Inst.* 20, 228(1922).—An infusion of the seeds injected subcutaneously into a guinea-pig produced no ill effects. Large doses of the meal are not eaten by animals. Small doses administered in mixt. with ordinary food to a dog and a goat produced slight diarrhea in 8-10 days; but the trouble disappeared on resumption of the normal diet. Roasting the seed destroys its toxicity.

A. P.-C.

Rhodesian grasses. ANON. *Rhodesian Agric. J.* 19, 134(1922); *Bull. Imp. Inst.* 20, 355-7(1922).—An account of investigations which have now been in progress for 11 yrs. concerning the improvement of Rhodesian pastures, dealing with the compn., feeding value, description and field characteristics of grasses of agricultural importance in S. Rhodesia.

A. P.-C.

Utilization of butyric esters [in foods] (FLORIANE) 17. Use of sodium 1-naphthol-2-sulfonate for the spectrophotometric estimation of aromatic amino compounds (MATHEWSON) 7. Antiscorbutic property of fruit. Apples and bananas (GIVENS, *et al.*) 11E. δ , δ -Decylenic acid from butter (GRÜN, WIRTH) 10.

13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

The role of chemical analysis and of the laboratory in the foundry and in mechanical construction. ANDRÉ LÉVI. *Ann. chim. anal. chim. appl.* 4, 327-37(1922).—A lengthy discussion of the need of close chem. control of all materials and processes.

C. C. DAVIS

The control of works operations by scientific instruments. LEONARD LEVY. *Chem. Age* (London) 7, 734-7(1922).—A brief outline of the application to works control of the X-ray tube, refractometers, spectrometers, viscosimeters, pyrometers and the like.

W. H. BOYNTON

Earning power of research as demonstrated by the experience of the American Rolling Mill Company. D. M. STRICKLAND. *Ind. Eng. Chem.* 15, 78-9(1923).—By adequate support of a no. of research problems, it is contended that at least 1 problem will be successfully solved and repay the entire research expense.

C. C. DAVIS

Chemical patents. E. FOURNEAU. *Chimie et industrie* 8, 1125-33(1922).—A discussion of "process patents" and "product patents," more particularly with relation to pharmaceutical products.

A. P.-C.

Evaporation.—Study of the various operating cycles in triple-effect units. A. L. WEBRE. *Chem. Met. Eng.* 27, 1073-8(1922).—A triple effect evaporator is assumed to be fed with 100,000 lbs. per hr. and to evap. 70,000 lbs. per hr. Steam used is 5-lb. gage, and vacuum is 26 in. Heat balances are calcd., showing feeding by the 3 general methods. Charts are given, showing the steam consumption and evapn. for different methods of feed and different feed temps. For the conditions assumed, use "parallel current" or forward for temp. of feed above 175° F., "countercurrent" or backward for temp. of feed below 125° F., "parallel feed" for temps. from 125° to 175° F. In general, cold feed calls for "countercurrent" operation, hot feed "parallel current" operation, and mild feed temp. "parallel feed." A list of items to be considered in *evaporator design* are given. It should be noted that changing the ratio of feed to evapn. will alter the conclusions from the above assumed conditions.

L. A. PRIDGON

Efficiency in centrifugal draining. T. J. DRAKELEY AND L. H. WILLIAMS. *J. Soc. Chem. Ind.* 41, 347-8T(1922); cf. C. A. 16, 977.—Using a 14-in. Spratt centrifuge

and spinning a charge of crystals of less than $\frac{1}{8}$ in. diam. for 15 min. gave an efficiency of 70.6% at 476 r. p. m. and only 73.5% at 1198 r. p. m. By efficiency is meant the percentage of the total mother liquor which has been extd. Enormous speeds are of doubtful advantage. In works practice it is advisable to maintain a low speed until the fluidity is reduced, and a higher speed to complete the removal of the liquor.

A. C. LANGMUIR

Lubrication of lubricants. LEONARD ARCHBUTT. *J. Soc. Chem. Ind.* 40, 287-93T(1921).—A review of work on ideal lubrication, the effect of pressure upon the viscosity of lubricating oils, the property of "oiliness" and its measurement. Bearings lined with white metal carry double the load carried by plain bronze bearings without increase in friction. Solid lubricants and the nature and thickness of the lubricating film are discussed.

EUGENE C. BINGHAM

The measurement of stirrer performance. J. C. WOON, E. R. WHITTEMORE AND W. L. BADGER. *Chem. Met. Eng.* 27, 1176-9(1922).—Tests were run on a 500-gal. wood tank with a single paddle stirrer. Samples were drawn continuously from 4 points in the tank, and each of these streams went through an elec. cond. cell. These cells were in series electrically, were adjusted to equal resistance, and a voltmeter was connected across each. Salt soln. was added to water in the main tank, and the time of complete stirring taken as the time when the current through these cells was a max. This was slightly longer than the time for the voltmeters to return to uniform readings. In the tank above described, stirring was complete in 1 min. or less at all speeds above 20 r. p. m. Above this speed there was a very rapid rise in net power consumption and no decrease in time of stirring. The water in the tank at all speeds seemed to be rotating as a homogeneous mass, without eddies or cross-currents.

W. L. BADGER

Heat-insulating materials. W. NEWTON BOOTH. *Gas. J.* 160, 798-9(1922).—Some of the uses and physical properties of the common insulating materials are given.

J. L. WILEY

Ruth's steam regulator in the chemical industry. R. HEYM. *Chem.-Ztg.* 46, 1105-6(1922).

J. H. MOORE

Some frequently met errors in cost analysis. W. A. BREEN. *Chem. Met. Eng.* 27, 1224-5(1922).

C. T. WHITE

DA PONTE, M. *Distillazione*. Milan: U. Hoepli. 847 pp. L 3750. Reviewed in *Boll. chim. farm.* 61, 255(1922).

FLEMING, A. P. M. and J. G. PEARCE. *Research in Industry*. London: Sir Isaac Pitman & Sons. 244 pp. 10s. 6d. Reviewed in *Electrician* 89, 541(1922).

Handbook of Chemical Engineering. 2 Vols. Edited by Donald M. Liddell. New York: McGraw Hill Book Co. \$8. Reviewed in *Chem. Met. Eng.* 27, 1184. (1922).

HART, EDWARD. *Textbook of Chemical Engineering*. 2nd Ed. revized. Easton, Pa.: Chemical Publishing Co. 241 pp. \$4. Reviewed in *Chem. Met. Eng.* 27, 757(1922).

PARNICKE, A. *Die maschinellen Hilfsmittel der chemischen Technik*. 4th ed. Revised and enlarged. Berlin: Paul Parey. M250. Reviewed in *Edel-Erden und Erze* 3, 103(1922).

WOLLASTON, T. ROLAND. *Filtration*. London: Sir Isaac Pitman & Sons, Ltd. 102 pp. 2s. 6d. Reviewed in *Chem. News* 125, 270(1922).

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

Paris water supply. ANON. *Engineering* 117, 573-6, 639-40(1922).—A brief history is given of the development of the Paris water system. The Paris water supply is now on 2 distinct systems. The first, "Service Privé," supplies potable water from 2 origins, springs at a distance or filtered water from the Seine and the Marne rivers. The amt. of water taken from the two sources varies, and depends upon existing conditions. The second system, "Service Public," for non-potable uses, supplies raw water taken from the Ourcq, Seine and Marne in sep. mains. The spring water (about 70,000,000 gals. per day) comes from the Dbuis, Vanne, Avre, and Loing and Lunain supplies. The filtered water, from the river Marne at St. Maur, and the river Seine at Ivry, is sterilized after filtration by O_3 or by $Ca(OCl)_2$ and is then pumped into the potable H_2O supply. The raw H_2O supply comes from a number of pumping stations, which draw from the Seine and which have a capacity of about 175,000,000 gals. per day and deliver into special reservoirs for distribution. Brief descriptions of the various installations used in connection with the different systems and of the process used for the purification of the river H_2O are included.

H. D. CARTER

Contamination of water samples with material dissolved from glass containers. W. D. COLLINS AND H. D. RIFFENBURG. *Ind. Eng. Chem.* 15, 48-9(1923).—Glass bottles were filled with distd. H_2O , tap H_2O , and a soln. of Na_2CO_3 (0.5 g. per liter). Good bottles did not dissolve enough in 1 to 6 mo. to cause any detectable change in the ordinary mineral analysis, while enough glass was dissolved from poor bottles within a week to change the character of the water. The greatest changes were the increase in SiO_2 and Na, and the change of alky. from HCO_3 to CO_3 and OH. Distilled H_2O produced the greatest solvent action.

C. C. BAKER

Use of steel pipe in water works. C. A. ELLIOTT. *J. Am. Water Works Assoc.* 9, 839-45(1922).—Cast-iron mains for general use in the distributing system are preferred but for larger feeder mains and pipe not subject to frequent disturbance plate metal or steel pipes have many advantages. Modern welding methods have done much to popularize the use of steel pipe. Steel pipes in use show satisfactory condition after long periods of service.

D. K. FRENCH

Standard specifications for pressure water filters. ANON. *J. Am. Water Works Assoc.* 9, 928-30(1922).—Two gals. per sq. ft. per min. are specified for all supplies used for drinking or for the prepn. of food products. Other rates are given to apply in special cases of treatment, filtration, etc. Tables of filter capacities for various rates are given.

D. K. FRENCH

Report of committee on revision of standard specifications for cast-iron pipe and special castings. F. A. BARBOUR, et al. *J. Am. Water Works Assoc.* 9, 916-20(1922).—The committee is not yet ready to recommend any definite revision. Most of the discussion relates to chem. specifications and the feasibility of including them. Methods of coating pipe will be considered.

D. K. FRENCH

Substitutes for pipe joints. ANON. *J. Am. Water Works Assoc.* 9, 868-73(1922).—The merits of leadite, a material less expensive than lead, are discussed. It comes in the form of a black powder, melts readily and is easily and quickly applied. With highly corrosive water it has not been found as satisfactory as lead. All experiences do not show equally satisfactory results.

D. K. FRENCH

Cast-iron water pipe for pressures higher than allowed by current specifications. C. E. INMAN. *J. Am. Water Works Assoc.* 9, 851-6(1922).—A factor of safety of 5 is considered ample to cover faults of manuf., danger of handling, and shock under use.

The Assoc. specifications are slightly over this factor. Discussion covered experiences in pipe up to 12 in. D. K. FRENCH

Investigations into the working of a slow-filtering sand filter in the tropics. P. C. F. v. Mededeel. Burgerlijken Geneeskundigen Dienst in Nederlandsch-Indie. Part 3, 135-66(1922); *Pub. Health Eng. Absts.* Dec. 16, 1922.—Expts. with slow sand filters at Weltevreden, Dutch East Indies, indicated (1) the importance of protozoa as a factor in the efficiency of slow sand filters under tropical conditions, (2) the disturbing influence of insects, crabs, etc. by their boring through the surface film, and (3) the beneficial effect of sunlight on purification, provided it is not present in sufficient amts. to promote the growth of algae. When H_2O artificially infected with *B. prodigiosus*, *B. typhosus* and *V. cholerae* was passed through a slow sand filter one out of 530,000 *B. prodigiosus*, one out of 750,000,000 *B. typhosus* and less than the latter named proportion of *V. cholerae* passed through. This process is feasible for the tropics with careful control, but on account of its inability satisfactorily to clarify waters rapid-sand filtration followed by sterilization with O_3 or Cl is preferred. Treatment with an excess of CaO , with adjustment of excessive causticity by use of CO_2 is also mentioned as a method of sterilization. G. C. BAKER

Boutron Boudet soap solution. A. M. BUSWELL. *J. Am. Water Works Assoc.* 9, 892-8(1922).—This soap soln. is 4 to 5 times as strong as that specified by Standard Methods of the A. P. H. A. It is used largely in testing the results obtained with the zeolite water softeners. Methods for prepg. the soln. are given in detail. D. K. F.

Tastes and odors. ANON. *J. Am. Water Works Assoc.* 9, 899-905(1922).—The organisms producing tastes and odors (*Englena*, *Peridinium*, *Anabaena*, giving a fishy and oily taste, and *Arcella*, a grassy or moldy taste) in reservoir waters are discussed. Many others are referred to. $CuSO_4$ alone is not always successful in eliminating these objectionable effects, but coupled with aeration it gives good results. D. K. FRENCH

The susceptibility of the egg masses of *Planorbis* to drying, chemical fertilizers, etc., and its bearing on the control of bilharzia disease. M. KHALIL. *J. Trop. Med.* 25, 67-9(1922).—Drying was the most potent agent in destroying the snails and eggs. In pools and puddles treatment with $CuSO_4$ is effective. W. A. P.

Boiler feed water as it ought to be—zero soft. ERNEST ROWE. *Blast Furnace & Steel Plant* 10, 647-8(1922).—A permutite zeolite water softener installed 3 yrs. ago in the Curtice & Co. plant of Bergen, N. Y. has eliminated troubles due to boiler water as well as boiler repairs. Other advantages of using zero-hardness water for boiler feed are given. H. D. CARTER

Review of the various methods for purifying boiler feed water. B. PREU. *Wärme und Kälte Tech.* 24, 197-201(1922).—Included is a new method for making use of feed water conig. many sol. salts. A certain percentage of water is drawn continuously from the boiler, passing to an evaporator where it evaps. at atm. pressure, giving distd. water which is returned to the boiler. It then passes through a heat exchanger, where it warms the feed water. In this way a moderate concn. of salts in the boiler water is obtained with economy of heat. ERNEST W. THIELE

Use of Illinois waters in Wabash locomotive boilers. O. W. CARRICK. *J. Am. Water Works Assoc.* 9, 906-16(1922).—The use of Na_2CO_3 to remove permanent hardness and frequent blowing off to remove the carbonate sludge are recommended for the prevention of foaming. The main item of expense involved is in blowing down. Reduction in engine failures, fuel consumption and stay-bolt breakage is claimed. Discussion questioned whether scale could be eliminated or foaming controlled by such practice. D. K. FRENCH

The two-story sewage-purification tank; its design and operation. A. C. HEWITT. *Commonwealth Eng.* 10, 125-8(1922).—Development of the process of septic treatment of

sewage is detailed. The design of Imhoff tanks with its adjuncts is dealt with under the heads of preliminary screening, grit chamber, tank proper and sludge beds. Particular attention is paid to the construction and operation of such a plant.

G. C. BAKER

Sewage disposal for North Side Chicago. H. P. EDDY, G. W. FULLER AND T. C. HATTON. *Nations Health* 4, 705-8(1922); cf. C. A. 16, 3934.—Recommendations for the discharge of sewage and of effluent from the treatment works are given. A plant of sufficient area and capable of removing the suspended solids, oxidizing the remaining org. matter and producing a comparatively stable effluent should be completed soon. The projects which seemed suitable (1) Imhoff tank-trickling filter works, and (2) activated-sludge treatment works were studied in detail. The Imhoff tank-trickling filter works provided for the passage of the sewage through coarse racks or screens, then through grit chambers followed by sedimentation in 2-story tanks, the effluent to be passed through fine screens before being discharged through nozzles over the surface of the trickling filters. The effluent from the trickling filters was to be passed through settling or humus tanks. The sludge from the digestion tanks was to be withdrawn at frequent intervals and dried on sludge beds. The activated-sludge treatment consisted of coarse screening, passing through grit chambers and treatment by aeration followed by sedimentation. Two methods were considered for the disposal of the activated sludge: (1) dewatering and drying, and (2) lagooning. Designs and estimates of cost of the proposed projects are given in detail. Because of the possibility of objectionable odors from Imhoff tank-trickling filter works and because an equal degree of purification can be obtained at substantially the same cost, the activated-sludge method is recommended for the sewage disposal. A feature of the recommendation is that the sludge be disposed of by lagooning until better methods of dewatering and drying the sludge are devised, thus abandoning, for the present at least, the hope of obtaining returns from the sludge for use as a fertilizer.

G. C. BAKER

Recent developments in sewage treatment. G. W. FULLER. *Am. Soc. Munic. Imp't.* 1922; *Munic. County Eng.* 63, 148-58(1922).—F. reviews the field of treatment covering skimming tanks to remove grease and matches, fine screening, types of screens, disposal of screenings (by dumping at sea, burial or incineration), Imhoff tanks, sep. sludge-digestion tanks, single-story tanks in rotation, plain sedimentation with continuous sludge removal, contact beds, trickling filters, activated-sludge and electrolytic processes. The sewage situation at Lima, Ohio, is also discussed (cf. C. A. 17, 167).

LANGDON PEARSE

A note on the silica content of some factory dusts. T. A. WEBSTER. *J. Ind. Hyg.* 4, 305-6(1922).—The amt. of free SiO_2 found in dusts from boot and shoe and from hosiery factories did not exceed that in lab. dust or in dust from a London house. (Total SiO_2 , 8.2-20.5%, free, 3.0-8.0%.) The responsibility for the incidence of phthisis in boot and shoe makers cannot be placed upon SiO_2 .

H. B. LEWIS

The use of hydrocyanic acid for the destruction of rats, parasites and insects. ED. BONJEAN. *Rev. Hyg.* 44, 776-794(1922).—Two processes of fumigation were tested on ships. Both were based on the liberation of HCN from NaCN by H_2SO_4 . The actual yield of HCN was much less than the theoretical, owing to soln., etc. The dose was 3 g. NaCN per m^3 for empty spaces; 7 g. per m^3 for cabins. Foodstuffs, including eggs, exposed to gas for a few hrs. took up HCN. The danger of the processes is emphasized.

JACK J. HINMAN, JR.

Heat economy in the chemical industry (boiler feed water meters) (GERMER) 1.
Ozone generator (U. S. pat. 1,437,302) 1.

GARNET, WILLIAM. A Little Book on Water Supply. Cambridge, Eng., University Press. 144 pp. 7s.

Sterilizing attachment for water-supply pipes. W. S. BACHMAN. U. S. 1,435,790, Nov. 14. The device serves to supply proportioned amts. of Cl or other sterilizing agent to the H₂O as it passes through the pipe.

Apparatus for sedimentation, dewatering and drying of sewage sludge. J. P. BALL. U. S. 1,434,520, Nov. 7.

Preventing scale formation in steam boilers or other apparatus. K. SCHNETZER. U. S. 1,436,686, Nov. 28. See Brit. 174,905 (C. A. 16, 1842).

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

Annual report of the Gurdaspur Agricultural Station for the year ending June 30, 1921. M. SULTAN ALI. *Rept. Operations Dept. Agr., Punjab 1920-21*, Part 2, 114-45.—Tables show the % of juice, glucose, sucrose, and total solids in different varieties of sugar cane, at intervals during the winter months. The analyses varied with the different types of cane.

K. D. JACOB

Annual report of the agricultural chemist to government, Punjab, for the year ending June 30, 1921. P. E. LANDER. *Rept. Operations Dept. Agr., Punjab 1920-21*, Part 2, 37-51.—Tables show (1) the effect of gypsum, in conjunction with castor cake and green manures, on the yield of wheat; (2) the fixation of N in cultivated and uncultivated Punjab soils; (3) the effect of the green manures, bhanga and guzra, on the yield of wheat; (4) the changes occurring in the glucose and sucrose content of different varieties of sugar cane during the winter months; and (5) the permeability and av. diam. of particles of different soils packed at different pressures. N fixation results were inconclusive. A new method for the detn. of the av. diam. of soil particles is mentioned. Full details will be published at a later date.

K. D. JACOB

Soil types as a basis for soil investigations. P. E. BROWN. *J. Am. Soc. Agron.* 14, 198-206 (1922).—An accurate scientific classification of soil types used in expts. is needed.

F. M. SHEERTZ

Investigation of bog soils in Polderen and lakes east of Utrechter Vecht, in connection with plans for the drainage of these lakes. Contribution to our knowledge of the chemical composition of swamp soils. D. J. HISSINK. *Intern. Mitt. Bodenk.* 11, 166-83 (1921).—Partial chem. analyses are given for a number of swamp soils of Holland, most of which are very high in org. matter. The problems involved in the drainage and fertilization of these soils are discussed.

M. S. ANDERSON

The influence of physical soil factors and of various fertilizer chemicals on the growth of the carnation plant. F. R. PEMBER AND G. E. ADAMS. Rhode Island Agr. Expt. Sta., *Bull.* 187, 94 pp. (1921).—The addition of 5.5 tons of limestone per acre to soil and manure had no marked effect on the growth of carnations nor did it promote chlorosis, while the addition at intervals during the season of over 1300 pounds of FeSO₄ per acre to the limed soil and manure depressed the production of flowers without improving the color of the foliage. There was no apparent difference from the use of Ca(NO₃)₂ or (NH₄)₂SO₄. The application of 800 lbs. of N as (NH₄)₂SO₄ increased the lime requirement by the Jones method 2100 lbs. over that where Ca(NO₃)₂ was used. The absorption of K and N was greater than P by the carnation plant. The nutritional needs are probably supplied when the dry material contains about 2% N, 0.5% P₂O₅, and 1.5 to 2% K₂O. The relation of N, P₂O₅ and K₂O as found in many plants was about 4 : 1 : 6.

J. J. SKINNER

Is chemical analysis a failure? R. R. SNOWDEN. *Citrus Leaves* 2, No. 5; 3, 23-4 (1922).—The apparent failure of chem. analysis in detg. the fertilizer needs of soils is due to (1) negligence on the part of the soil analyst, (2) use of a too drastic method for making the soil solution for analysis, thereby showing large values in plant foods not available to the crop, (3) limiting plant-food needs to K, P_2O_5 and N, ignoring the other necessary elements, (4) overlooking fresh limitations by a new limiting factor after correction of a former one, (5) neglect of the character of combinations in which the plant-food elements occur, (6) overlooking direct and indirect effects of undetd. elements, (7) disregard of the physical status of the soil, or some error of treatment not referred to the soil.

J. J. SKINNER

Trend of modern fertilizer plant construction. P. S. GILCHRIST. *Ind. Eng. Chem.* 15, 86-7 (1923).—The requirements for construction of a modern fertilizer plant and a description of manipulation of equipment and handling of materials are given.

J. J. SKINNER

Fertilizers for Maryland soils. A. G. MCCALL. Maryland Agr. Expt. Sta., *Bull.* 247, 117-161 (1921).—Fertilizer formulas for several soil types for various crops and directions for prep. certain formulas from raw materials are given together with a rept. of the fertilizer expts. conducted on various soil types in Maryland.

J. J. SKINNER

Report of committee on vegetation tests on the availability of phosphoric acid in basic slag. H. D. HASKINS, et al. *J. Assoc. Official Agr. Chem.* 6, 123-4 (1921).—Four slags were tested by expt. stations. The P_2O_5 in each slag was freely available to the crops grown; the results compare favorably with those obtained with acid phosphate, both from the standpoint of yield of crop as well as in P_2O_5 recovered. The tentative Wagner method when used on basic slag phosphates gives about the same proportion of available P_2O_5 in this class of products as does the official neutral NH_4 citrate method when used on acid phosphate or superphosphate; both methods give results which compare favorably with results obtained by vegetation pot work. The tentative Wagner method is a reliable procedure for measuring the available phosphoric acid in basic slag phosphates.

J. J. SKINNER

Conditions for the practical use of calcium cyanamide as a fertilizer. P. MAZE. *Compt. rend.* 175, 1093-6 (1922).— $CaCN_2$ together with peat gave marked increase in crop yield over that obtained with peat alone and in many cases greater than when $(NH_4)_2SO_4$ was used with peat. A sandy soil showed greater benefit than a clay soil from the use of peat and cyanamide. Larger amts. than 4000 kg. of peat per hectare increased the acidity to a point where the hydrolysis of the cyanamide was retarded.

M. S. ANDERSON

The comparative assimilability of tricalcium phosphate and the phosphates of aluminium and iron. CH. BRIEUX. *Compt. rend.* 175, 1096-9 (1922).—One % citric acid serves as a much better solvent of P_2O_5 in soils than 0.5% HNO_3 . The phosphates of Al and Fe are much more sol. than $Ca_3(PO_4)_2$ in NH_4 citrate. In citric acid and HNO_3 $Ca_3(PO_4)_2$ is more sol. Pot expts. with $Ca_3(PO_4)_2$ and phosphates of Al and Fe showed in most cases that Al phosphate stimulated the production of dry matter to the greatest extent, and that Fe phosphate had the least effect. The av. P_2O_5 content of plants was much higher when Al phosphate was used than in the check or the other treatments.

M. S. ANDERSON

Calcium nitrate in agriculture. MAURICE BOUSQUET. *Prog. agr. vii.* 78, 545-7 (1922).—A discussion of the value of $Ca(NO_3)_2$ as compared with other nitrate sources, and the soil and crop conditions to which it is particularly adapted. $Ca(NO_3)_2$ gave an increased yield with several crops.

P. R. DAWSON

Thirty years' experience with sulfate of ammonia. F. W. MOYSE. *Mass. Agr.*

Expt. Sta., *Bull.* 204, 84-98(1921).— $(\text{NH}_4)_2\text{SO}_4$ has been effective as a fertilizer when accompanied by an application of lime. In the absence of lime it has sometimes been injurious, owing to the formation of sol. compounds of Mn, Al and Fe. Injury has been greatest in dry periods when the lessened soil moisture becomes more concd. with sol. salts. $(\text{NH}_4)_2\text{SO}_4$ has been particularly effective on the cereals. It gave very good results with mixed grasses, good results with uninoculated soy beans, only slightly increased yields of clover and none with potatoes. $(\text{NH}_4)_2\text{SO}_4$ is about 0.9 as effective per unit N as NaNO_3 . J. J. S.

The effect of Bordeaux mixture upon the chlorophyll content of the primordial leaves of the common bean, *Phaseolus vulgaris* L. W. A. RUTH. *Am. J. Botany* 9, 535-50(1922).—The primordial leaves of the bean sprayed with Bordeaux mixt. do not grow as large as unsprayed leaves. The chlorophyll content per unit area is slightly increased by the spray. The chlorophyll content per unit is decreased as the leaves develop after shedding the cotyledons. The chlorophyll of the young primordial leaves is lower than that of the primordial leaves just after the shedding of the cotyledons. J. J. SKINNER

Treatments against *Cochylis* (vine worm) in 1921. H. FAES AND M. STAEBELIN. *Prog. agr. vit.* 78, 326-30, 350-3(1922).—Soap-pyrethrum and nicotine-Cu sprays are most effective in combating *Cochylis*. The lasting effect of soap-pyrethrum renders it preferable for use against the 1st generation of the parasite, since nicotine preps. must be applied at a critical time. Nicotine, however, gave the best results in combating the 2nd generation. P. R. DAWSON

Cultivation of pyrethrum (*Pyrethrum cinerariaefolium*) in France. H. FAES. *Prog. agr. vit.* 78, 394-400(1922).—A description of the present development of the industry, mode of culture, harvesting of the plant, and utilization of the products. P. R. DAWSON

Investigations of the cultivation of pyrethrum and the insecticidal properties of soap-pyrethrum. A. JUILLET. *Rev. vit.* 57, 310-13(1922).—A review. P. R. D.

Experiments in combating *Eudemis* with the soap-pyrethrum prepared by the faculty of pharmacy of Montpellier. RENÉ SALOMON. *Rev. vit.* 57, 188-90(1922).—At a diln. of 0.01 the soap-pyrethrum prepn. was equal in effectiveness to a com. prepn., "Truffaut," causing a mortality of 75-80%. At a diln. of 0.02 the destruction was complete. The great advantages of its properties of wetting, adherence, and penetration were demonstrated. No objectionable residue remained on the crops, and no injury to foliage resulted, even during the hottest time of day. P. R. DAWSON

16—THE FERMENTATION INDUSTRIES

C. N. FREY

Flocculation of yeast and the effect of pure cultures. K. GEYS. *Z. ges. Brauw.* 1922, 51-3, 57-60; *Chimie et industrie* 8, 1099(1923).—Deterioration of yeast kept for some time in yeast app. is due to a gradual decrease in the flocculating power of the yeast. Successive samples taken from the pure culture app. showed a marked and increasing tendency to remain in suspension in the fermentation vats at the end of the fermentation, instead of settling out rapidly in compact masses. Dusty yeast, i. e., yeast which does not settle rapidly, gives a beer with a lower acidity. Microscopic examn. shows that this yeast is in poor physiological condition, contg. 20-30% of dead cells. Deterioration may be explained by assuming that a long stay in the pure culture app. exhausts the yeast. To prevent it, the app. should be charged with a sufficiently concd. wort. Observations on the effects of an elec. current on the migra-

tion of yeast cells show that cells at rest are positively charged and active cells are negatively charged. During fermentation the cells remain negatively charged for the first few days; but as their activity decreases they become neutral, and it is at this stage that flocculation occurs. Pulverulent yeast also loses its negative charge when its activity ceases; so that its inability to settle out must be attributed to some other cause. Settling properties may be due to the presence of a sort of envelope, formed of glutinous matter, which surrounds the cells and renders their agglomeration possible. A. P.-C.

The use of cane molasses in yeast growing. F. WENDEL. *Z. Spiritusind.* 45, 306(1922).—Because of a shortage of beet molasses investigations were made to det. the value of cane molasses in yeast growing. It is similar to beet molasses in sugar content but higher in P and lower in N. By heating dil. cane molasses, adding phosphates and making the soln. alk., a good yeast-growing medium is produced. Yeast grown in treated molasses has good color and excellent keeping qualities. C. N. FREY

"Sulfite" alcohol. R. DELABY. *Bull. sci. pharmacol.* 587-91(1922).—A review.

F. S. HAMMETT

Hydrogen-ion concentration in brewing. W. WINDISCH, W. DIETRICH AND P. KOLBACH. *Wochschr. Brauerei* 39, 67(1922); *Chimie et industrie* 8, 1009(1922); cf. *C. A.* 16, 2955.—The org. indicators used in Michaelis' method for the detn. of H-ion concn. (*C. A.* 16, 1469) are light-sensitive and bleach out in time. Suitable mixts. of K_2CrO_4 and $K_2Cr_2O_7$ can advantageously replace Michaelis's solns. for the prepn. of the color scales. The primary solns. are 0.1 N $K_2Cr_2O_7$ (4.903 g., previously heated to 130°, per l.) and 0.1 M K_2CrO_4 (19.44 g. per l.), from which are prepd. 0.02 N and 0.01 M solns., resp. Water distd. over $KMnO_4$ should be used. The following tables give the data required for prepg. the scales used in the Michaelis' method:

Scale for replacing α -dinitrophenol									
cc. 0.01 M K_2CrO_4	3.9	2.9	4.7	3.5	2.5	1.7	1.2	0.9	0.5
cc. water	10	10	20	20	20	20	20	20	20
pH =	4.4	4.2	4.0	3.8	3.6	3.4	3.2	3.0	2.8
Scale for replacing γ -dinitrophenol									
cc. 0.02 N $K_2Cr_2O_7$	4.5	3.3	2.6	3.8	2.6	1.7	1.1	0.7	
cc. water	10	10	10	20	20	20	20	20	
pH =	5.4	5.2	5.0	4.8	4.6	4.4	4.2	4.0	
Scale to replace p -nitrophenol									
cc. 0.01 M K_2CrO_4	10.0	7.5	4.9	2.9	1.8	2.6	1.7	1.0	0.8
cc. water	10	10	10	10	10	20	20	20	20
pH =	7.0	6.8	6.6	6.4	6.2	6.0	5.8	5.6	5.4
Scale to replace m -nitrophenol									
cc. K_2CrO_4	8.0	7.0	4.0	2.5	1.5	2.0	1.4	1.1	
cc. $K_2Cr_2O_7$	2.5	1.6	1.0	1.0	0.5	0.5	0.2	0.1	
cc. water	10	10	10	10	10	20	20	20	
pH =	8.4	8.2	8.0	7.8	7.6	7.4	7.2	7.0	

These scales are very stable and showed no change in color after exposure to sunlight and to arc light. A. P.-C.

Cooling and flocculation of wort. E. EMFLANDER. *Wochschr. Brauerei* 39, 67 (1922); *Chimie et industrie* 8, 1098(1922).—The shape of the cooler and the method of flow of the wort have but little influence. If wort is allowed to stand for some time after boiling, a very thin film will form on the surface, which is formed of the substances which lower the surface tension of the wort. To obtain as complete a sepn. as possible of these coagulable substances, the wort should stand half an hour after boiling, with stirring from time to time to break the film. A similar phenomenon occurs when the wort reaches the cooling vat, and here also it is advisable to agitate intermit-

tently. Continuous agitation detrimental, preventing the formation of the film and elimination of the coagulable matter. Appreciable flocculation on the cooler, has not been obtained as the movement of the liquid is too rapid and does not permit agglomeration of the particles. A certain amt. of flocculation is observed only where the wort is at rest, and most of the time this is negligible. A. P.-C.

Determination of carbon dioxide in beer by precipitation. G. BODE AND K. HEMBD. *Wochschr. Brauerei* 39, 43(1922); *Chimie et industrie* 8, 1098(1922).—B. and H. make certain modifications in Macheleidt's methods for the detn. of CO_2 in beers (C. A. 16, 2954), which consists in fixing CO_2 with NH_3 , sepg. P_2O_5 with magnesia mixt., converting the $(\text{NH}_4)_2\text{CO}_3$ into CaCO_3 by adding an excess of CaCl_2 and detg. the CaCO_3 by the usual methods. The cold filtration of the P_2O_5 is difficult, and with dark beers it cannot be carried out. The liquid should be brought to boiling and filtered hot. Instead of pptg. the whole of the CO_2 in the filtrate by CaCl_2 , it is preferable to work on an aliquot, in which case the ignition of the CaCO_3 is easily carried out in a Pt dish on a Teclu burner (cf. next abstract). A. P.-C.

Determination of carbon dioxide in beers. G. MACHELEIDT. *Wochschr. Brauerei* 39, 73(1922); *Chimie et industrie* 8, 1098(1922); cf. preceding abstract.—Heating causes decompn. of $(\text{NH}_4)_2\text{CO}_3$ and appreciable loss of CO_2 . Rapid filtration can be obtained if care is taken not to add too great an excess of NH_3 ; 10 cc. of 25% CO_2 -free NH_3 can fix all the CO_2 in one-third of a l. of beer. The use of an aliquot instead of the whole filtrate is of minor importance. M. obtained entirely satisfactory results with porcelain and quartz dishes; but certain precautions are necessary. A. P.-C.

The diastatic power of Czecho-Slovak malts. F. DUCHACEK. *Wochschr. Brauerei* 39, 25-7(1922); *Chimie et industrie* 8, 1097-8(1922).—D. examd. a number of Czecho-Slovak malts, and considers the diastatic power sufficiently high to permit of their being used in admixt. with raw grain. A. P.-C.

Vertical malt kilns. G. KROFFE. *Wochschr. Brauerei* 39, 100(1922); *Chimie et industrie* 8, 1100(1922).—The main advantage of vertical malt kilns is ease of charging and emptying. In the ordinary kiln, properly operated, there is better utilization of space, improved aeration, less shattering of malt sprouts and consequently a better quality of malt. A. P.-C.

Rapid determination of sulfur dioxide (in wine). R. MARCILLE. *Ann. fals.* 15, 398-401(1922).—To 10 cc. of wine in a wide-necked 250-cc. Erlenmeyer flask add 10 cc. of NaOH (80 g. per l.), evap. to half its vol., cool, add 100-150 cc. of H_2O , enough dil. H_2SO_4 to neutralize the NaOH , and 1-2 cc. of starch paste, and titrate with I equiv. to 1 or 2 mg. of SO_2 per cc. (4 or 8 g. I per l.). In the case of certain wines heating without eliminating alc. and aldehydes gives 200 mg. per l. less than the above method. The method is not suitable for wines contg. more than 5 g. of sugars per l. They are distd. in the presence of H_3PO_4 to caramelization, the distillate being collected in 10 cc. of NaOH (80 g. per l.) and treated as above. A detn. can be carried out in about 15 min. Duplicates on the same wine do not vary by more than 5%. A. P.-C.

The determination of pentosans. G. MACHELEIDT. *Wochschr. Brauerei* 39, 90(1922); *Chimie et industrie* 8, 1099(1922).—A. Jolles (*Ber.* 1906, 96) indicated a method similar to that of Ling and Nanji (C. A. 15, 3958), based on the fixation of the aldehyde with bisulfite and detn. of the excess of SO_2 by I. Jolles observed that the acidity of the solns. obtained by distn. of the pentosans with HCl was too high and prevented the quant. fixation of the furfural by the bisulfite. Consequently he modified Tollens' method, effecting the sepn. of furfural in the presence of 12% HCl , and steam distg. Sepn. of furfural is slower and 2,000-3,000 cc. must be collected to recover all the furfural. In order to obtain a furfural distillate free from acid and salts, M. proceeds as follows: Treat an amt. of sample corresponding to 0.05-0.2 g. of pentose with HCl

according to Tollens' method. Add a few drops of methyl red to the distillate, decolorize with NaOH and just bring back the color with HCl. Distil till NaCl begins to crystallize. Add 25–40 cc. of NaHSO_4 (5.2 g. per l.) to the distillate, let stand an hr., and titrate the excess of SO_2 with 0.05 N I (1 cc. = 0.00375 g. pentose, and 0.0083 g. pentosan).

A. P.-C.

Influence of the origin of soluble starch on the determination of the diastatic power of malt by Windisch and Kolbach's method. B. LAMPE. *Wochschr. Brauerei* 39, 31 (1922); *Chimie et industrie* 8, 1098(1922).—By an investigation into the detn. of the diastatic power of malts by Windisch and Kolbach's method, L. shows that the results vary considerably according to the nature of the sol. starch used. For comparative tests, it is important to use the same starch.

A. P.-C.

Tannin in whiskey. R. D. SCOTT. *J. Am. Pharm. Assoc.* 11, 1017–8(1922).—The amt. of tannin in whiskey is an important criterion in judging its purity. In 11 authentic specimens tannins varied from 0.30 to 0.425 g. per l. and in several specimens of "stretched" whiskey assayed about 0.1 g. per l. The method used, an adaptation of the Folin and Denis colorimetric method for the detn. of phenols in urine (C. A. 6, 3434), is as follows: Place 1 cc. of whiskey in a 100-cc. Nessler tube and make up to the mark with H_2O . Add 1 cc. of the F. and D. reagent and 5 cc. of a satd. soln. of Na_2CO_3 . After 10 min. the color is compared with controls contg. known amts. of tannin.

L. E. WARREN

The nipa palm as a source of sugar and alcohol (ANON) 23.

Yeast. T. B. WAGNER. U. S. 1,434,462, Nov. 7. Bakers' yeast is produced in a nutrient soln. in which "steep water" (resulting from the treatment of corn with a 0.33% soln. of SO_2 in H_2O) obtained as a by-product in the manuf. of starch, glucose or maltose is used as a source of nitrogen and mineral salt nutrition for the yeast, with various sugar sirups such as "refiners' sirup," cane molasses or glucose sirup and additional nutrient salts as found necessary, e. g., NH_4 phosphate.

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Investigation of the bark of *Tiliacora acuminata* Miers. L. VAN ITALLIE and A. J. STRENNHAUER. *Pharm. Weekblad* 59, 1381–8(1922).—The following constituents were isolated and identified: a new cryst. alkaloid *tiliacorine*, a non-cryst. alkaloid, *d*-quercitol, fumaric acid, a semi-drying oil, phytosterol, resin and glucose. *Tiliacorine* m. 260–1°, $[\alpha]_D^{25}$ 105.3° in 0.5 N HCl. With oxidizing agents ($\text{K}_2\text{Cr}_2\text{O}_7$, KNO_3 , $\text{K}_3\text{Fe}(\text{CN})_6$, MoO_3 , KMnO_4 , V_2O_5 , CeO_2 , H_2O_2 , but not KIO_3 or KClO_3) the soln. in H_2SO_4 turns blue and finally green. On the basis of elementary analysis, mol. wt. detn. and MeO detn. the formula is $\text{C}_{20}\text{H}_{27}\text{NO}_2(\text{OCH}_3)_2$.

A. W. DOX

Matriculation sheets. A. SCHAMELBOUT. *J. pharm. Belg.* 4, 775, 790–800, 835–836, 860, 918(1922).—Monographs intended for introduction into the Belgian National Formulary are given for basic Pb carbonate, Sb, dried egg albumin, strychnine sulfate, $\text{SrCl}_2 + 6\text{H}_2\text{O}$, strychnine, scopolamine-HBr, strychnine arsenate and K metantimonate.

A. G. DUMÉZ

The bitter principles of bops. GARRIGUES. *Répert. pharm.* 34, 322–4(1922).—G. reviews briefly the conflicting opinions in the literature on the identity of the bitter principles of bops. This uncertainty with respect to the chem. identity of these bitter

principles is the main reason why so little is known of their pharmacodynamic properties.

A. G. DuMaz

Fery's spectrograph and its utility in the determination of essential oils. J. BOYER. *Am. Perfumer* 17, 389-90(1922).—By this app., now greatly simplified in construction, instant and permanent spectrograms can be made to be kept as records. For essential oils (or perfumed liquids) the ultra-violet spectrum is used. The app. and its application are fully discussed.

W. O. E.

Utilization of butyric esters. M. FLORIANE. *Am. Perfumer* 17, 392(1922).—The specific application of the more important org. butyrates in foods and perfumes is discussed.

W. O. E.

Butyric esters and their uses in perfumery. P. MIRGODIN. *Perfumery Essent. Oil Record* 13, 385-6(1922).—The importance of various esters in perfumes is discussed, together with several formulas showing their application. (Cf. preceding abstract). Also in *Chem. Age* (London) 7, 856(1922).

W. O. E.

Chemistry of alkaloids. N. EVERS. *Chem. Age* (London) 7, 594-8(1922).—A review.

W. O. E.

Chemistry of synthetic drugs. J. B. COHEN. *Chem. Age* (London) 7, 600-3(1922).—A review of the application of org. chemistry in therapy.

W. O. E.

Santoveronin, the new vermifuge. A. MARK. *Chem.-Ztg.* 46, 992-3(1922).—The more important vermifuges are discussed. Santoveronin is alleged to unite the active principles (groups) of santonin and mail fern and to be effective in expelling all intestinal parasites. Cf. *C. A.* 15, 3723.

W. O. E.

Santoveronin. A. HERRMANN. *Chem.-Ztg.* 46, 1081(1922).—H. refers to the finding of inorg. constituents, notably Cu in relatively large amt., the presence of which the manufacturer (Cf. preceding abstract) totally ignores.

W. O. E.

Estimation of nicotine in tobacco and tobacco smoke. M. POPP and J. CONTZEN. *Chem.-Ztg.* 46, 1001-2(1922).—The results obtained in comparative nicotine detns. via Mach and Rasmussen show satisfactory agreement. Some expts. also are described looking to the detn. of pyridine as a possible constituent of tobacco exts. by pptn. with silicotungstic acid. The values found show this reagent inexact.

W. O. E.

Analysis of licorice root and licorice extract. P. A. HOUSEMAN. *J. Assoc. Official Agr. Chem.* 6, 191-6(1922).—Analytical methods are given for licorice root and ext., with further remarks on various constituents extd. by solvents and not detd. quant.

W. O. E.

Some recent work on anthelmintics. T. A. HENRY. *J. Soc. Chem. Ind.* 41, 467-9R(1922).—A review.

W. O. E.

Work on pimento-leaf oil in Jamaica. E. E. A. CAMPBELL. *Perfumery Essent. Oil Record* 13, 389-91(1922).—Pimento leaves yield slightly over 2% of crude oil, of which the eugenol content at certain seasons of the year and in different years may range from 95% to as low as 32%. The results from various distns. are shown in tabulated form.

W. O. E.

Manufacture of certain drugs for the treatment of leprosy. G. A. PERKINS. *Philippine J. Sci.* 21, 1-14(1922).—Recent developments in leprosy treatment are discussed from a chemist's viewpoint. The manuf. of chaulmoogra ethyl esters is described in detail. The prepn. of 6 other drugs, mostly following the procedure of other investigators, is described, these being the other medicines chosen by the Committee on Leprosy Investigation for exptl. treatment.

W. O. E.

Critical study of the new volumetric method of Kariyone and Kimura for the determination of santonin in worm-seed. G. FAVREL. *Bull. sci. pharmacol.* 29, 553-5(1922); cf. Kariyone and Kimura, *Chem. and Druggist*, August 13th, 1921, 1682, p. 57.—The

method failed to give concordant results when used on worm-seed and showed twice the values found by the grav. method. This occurred even when extra precautions were taken to get rid of all traces of CHCl_3 . These abnormalities are attributed to the extn. of resins or other substances by the CHCl_3 which are acted on by the NaOH .

F. S. HAMMETT

Preservation of commercial Javel water. A. GUILLAUME. *Bull. sci. pharmacol.* 29, 555-9(1922); cf. *C. A.* 16, 788.—When the containers of Javel water are protected from light by wrapping in black paper or are colored yellow, preservation is good.

F. S. HAMMETT

Liquid soap with formaldehyde. E. CORDONNIER. *Bull. sci. pharmacol.* 29, 559-62(1922).—305 g. of castor oil is saponified with alc. KOH 130 g. and 540 cc. 95% alc. Paraffin and pumice assist in preventing foaming and bumping. 300 cc. of H_2O is added and the alc. distd. off. The mixt. is cooled and about 400 g. of HCHO added and then distd. H_2O to make a total wt. of 5 times that calcd. for the soap. F. S. H.

Iodine-containing tablets. (Inorganic and organic). BOUVET. *Bull. sci. pharmacol.* 29, 569-78(1922).—A review.

F. S. HAMMETT

Solution of cresol soap. A. FREYMUTH. *Deut. Parfum. Ztg.* 8, 28-30(Feb. 25, 1922); *Chimie et industrie* 8, 1060(1922).—The cresol used in pharmacy is a mixt. of the three isomers. *m*-Cresol is slightly more toxic than PhOH , but has much stronger bactericidal properties. The following formula is given for emulsifying crude cresol: linseed oil 120, KOH 27, H_2O 41, alc. 12, crude cresol 200.

A. P.-C.

Salicylaldehyde in perfumery. L. ADELAIDE. *Riv. Ital. ess. prof.* 4, 27-8(1922); *Chimie et industrie* 8, 1062(1922).—A description of the Reimer and Tiemann process of manuf. of salicylaldehyde from PhONa and CHCl_3 , and of its properties. *Violettol*, which is used to fortify natural violet perfume, is a mixt. of 10% *ionone* and 90% salicylaldehyde.

A. P.-C.

Phenyl ethers. M. MURAT. *Parfumerie moderne* 15, 51-2(1922); *Chimie et industrie* 8, 1063(1922).—The most important of the phenyl ethers is Ph_2O , white crystals, m. 28° , b. undecomposed at 251° , used extensively in soapmaking. It is prepd. (1) by dry distn. of $(\text{PhO})_2\text{Al}$; (2) by passing PhOH vapors over Th oxide at 430° .

A. P.-C.

Characteristics and constituents of Cinnamomum glanduliferum. V. MASSERA. *Riv. Ital. ess. prof.* 4, 41-2(1922); *Chimie et industrie* 8, 1063(1922).—The leaves and twigs of *Cinnamomum glanduliferum* from Uris (Come Lake) yielded on steam distn. 0.6% of a clear, light-yellow oil, with a remarkable camphor-like odor, $d_{20}^{20} 0.9024$, $(\alpha)_D^{20} -23.20'$, $n_D^{20} 1.4685$, acid no. 0, sapon. no. 11.16, total alc. calcd. to $\text{C}_{10}\text{H}_{18}\text{O}$ 11.28%, total alc. as $\text{C}_{10}\text{H}_{18}\text{O}$ 11.34%; one part is sol. in 4.5 parts of 80% alc. at 22° . This oil probably contains camphor, 34.20% of cineole, and about 10% of terpineol. A. P.-C.

Paraform—a new insoluble local anesthetic. P. CHAMPALBERT. *Industrie chimique* 9, 498(1922).—"Paraform" is $p\text{-H}_2\text{NC}_6\text{H}_4\text{CO}_2\text{Bu}$. It possesses an appreciably greater anesthetic action than the other *p*-aminobenzoic esters; it does not methemoglobinize, and it is practically non-toxic. Dogs can stand, without trouble 1 g. per kg. of body wt. (through the stomach). From a theoretical standpoint it would have been interesting to det. if the Am ester was more or less active than paraform. C. made a thorough clinical investigation of paraform, and carried out various pharmacodynamic tests to ascertain its anesthetic power, both on dogs and on men.

A. P.-C.

Ethyl ether, its tests and stability. HUGO WASTESON. *Svensk Farm. Tids.* 26, 473-8, 490-1(1922).—Abs. pure water-free alc.-free ether has $d_{15} 0.718-0.719$. H_2O lowers the b. p. of ether and alc. raises it. Et_2O contg. 1.8% H_2O and 1.15% alc. has the same b. p. as pure Et_2O . Et_2O of sp. gr. 0.780 $b_{700} 34.45-34.7^\circ$. Care-

fully prepd. pure Et_2O does not give alk. reaction with indicators. The pure Et_2O was kept in a half-full bottle at room temp. for 3 mos. without any change in quality. The presence of alc. is of no advantage as regards the keeping qualities. Et_2O allowed to stand in a light bottle in direct sunlight is oxidized. There may be catalyzers present. Samples which have a slight KI test at the beginning will give a strong test later. Ether should not give any yellow color with KI soln. It is recommended for the Pharm. succ. that sp. gr. for Pharm. Et_2O be fixed at 0.718-0.722 and for anesthetic Et_2O 0.718-0.720. It is also recommended that the supply of Et_2O be stored over metallic Na.

A. R. ROSE

Method for the determination of arsenic in Pil. Acid. Arsenicos. AUGUST LÖNNSSON. *Svensk Farm. Tids.* 26, 508-10(1922).—Weigh the pills into a flask which has a glass stopper. Cover the sample with water and heat to complete soln. after which cool to 60° and make alk. by adding 3 g. $(\text{NH}_4)_2\text{CO}_3$. Then heat this soln. on a boiling water bath for 15 min. with the stopper in place. When again cool add HCl to faint acidity and then 1.5 g. NaHCO_3 and starch paste. Add 0.1 N I until the soln. is blue, then make just acid and add 35 cc. 25% HCl in excess. Add 5 g. KI and set aside for 15 min. Now titrate the soln. by adding an excess of standard $\text{Na}_2\text{S}_2\text{O}_4$, dil. to 100 cc. and titrate back with 0.1 N I. Correct the titer figures by blanks for I liberated by the reagents. Calc. As from the $\text{Na}_2\text{S}_2\text{O}_4$ used.

A. R. ROSE

American eosins. H. J. CONN, et al. *Science* 56, 689-90; *J. Am. Med. Assoc.* 79, 1711-2(1922).—A progress report of a committee which is investigating the quality of Am. dyestuffs used in biol. staining. The chem. nature of eosin is first discussed. The great diversity of eosins on the market makes the subject very confusing. Samples of different lots of eosin were submitted to collaborating histologists and bacteriologists who subjected them to various procedures. The samples of Am. make were found to be the best. A list is given which includes most of the important jobbers, from whom satisfactory eosins may be obtained.

F. W. T.

Investigation of purified siliceous earth. W. G. CROCKETT. *J. Am. Pharm. Assoc.* 11, 84-6(1922).—Eight samples were procured. Not one conformed to the U. S. P. requirements. One was too much adulterated to be considered. Each contained over 20 times as much Fe as the U. S. P. permits. Five contained org. matter. The material sol. in dil. HCl exceeded the U. S. P. limit. Six gave turbid filtrates after shaking with H_2O . Three were not fine powders but were gritty. One showed excess loss on ignition and one had a disagreeable odor. C. believes the product should be deleted from the next U. S. P.

L. E. WARREN

Oil of catnip. R. M. HIXON. *J. Am. Pharm. Assoc.* 11, 96-8(1922).—The specimens examd. were distd. in 1915 and 1916 and 1 specimen had been cohobated. The consts. were d_{20} 1.058, 1.047 and 1.076; $[\alpha]_D^{25}$ —, 5.59° and 2.25°; sapon. no. —, 319, 379; miscible in all proportions is 90% EtOH. The last 2 were sol. in an equal vol. of 80% EtOH and require 2.5 vols. of 70% EtOH for soln. The α_D decreases with the increase of the lactone content. The lactone was removed by shaking with NaOH, only 13% remaining. The non-lactone portion was distd. in steam. About 65% volatilized. The distillate had the odor of catnip oil; d_{20} 0.900, $[\alpha]_D^{25}$ —14.6°; n_D^{25} 1.4912; sapon. no. 24; sapon. no. (after acetylation) 84. The non-lactone portion contained a bicyclic sesquiterpene.

L. E. WARREN

The manufacture of synthetic medicinal chemicals in America. A. S. BURDICK. *J. Am. Pharm. Assoc.* 11, 98-108(1922).—A plea for the pharmacist to support the new industry in America.

L. E. WARREN

Hollyhock root (?) for Althaea. O. A. FARWELL. *J. Am. Pharm. Assoc.* 11, 184(1922).—The drug markets contain a malvaceous drug sold for marshmallow root which is not true *Althaea* although the pharmacognostic characters indicate that it is

closely related to *Althaea*. F. suggests that it may be *Althaea rosea*, the hollyhock.

L. E. WARREN

Source of balsam poplar buds. O. A. FARWELL. *J. Am. Pharm. Assoc.* 11, 184-5(1922).—The studies indicate that com. balsams of poplar buds are collected from *Populus balsamifera* Linn., *P. tacanahaca* Mill. and *P. candicans* Ait. No evidence was obtained to indicate that one of the sources of the drug is *Populus nigra* as the National Formulary states.

L. E. WARREN

The influence of methods of distillation on the commercial value of oil of American wormseed. G. A. RUSSELL. *J. Am. Pharm. Assoc.* 11, 255-62(1922).—Authentic chenopodium was grown, collected, dried and divided into 2 portions. With rapid distn. and the condenser warm 0.183% of oil was obtained. This conformed in all respects to the U. S. P. requirements. The 2nd portion was distd. slowly with the condenser cold. The yield was 0.123%. This oil did not conform in all respects to the U. S. P. tests. A field investigation of chenopodium oil distilleries revealed that most distillers used condensers with cold H₂O. Some operators admitted the steam slowly, allowing it to work up through the charge gradually. This tends to decompose the ascaridole in the oil. Most producers favor a change in U. S. P. standards for the oil but R. shows this to be unnecessary. If the distn. be carried out rapidly and the condenser kept warm (74°) the oil will generally be of good quality and the yield reasonably good.

L. E. WARREN

The assay of salicylic acid and official salicylates. ABRAHAM TAUB AND HARRY TAUB. *J. Am. Pharm. Assoc.* 11, 516-21(1922).—Various methods are compared. This is selected as most satisfactory. Dissolve about 0.4 g. of the substance in H₂O and dil. to 200 cc. Place 25 cc. of this soln. in a 250-cc. glass-stoppered flask and add an excess of 0.1 N Br-bromate soln., followed by 3 cc. of HCl. Insert the stopper. Allow to stand 20-30 min. with occasional shaking, remove stopper and add 5 cc. of 10% KI soln. and 1 cc. of CHCl₃. Shake until the ppt. is dissolved, rinse the neck with H₂O and titrate with 0.1 N Na₂S₂O₄, using starch soln. as indicator.

L. E. WARREN

What is aloes U. S. P.? E. N. GATHERCOAL AND R. E. TERRY. *J. Am. Pharm. Assoc.* 11, 523-6(1922).—The problem discussed is whether it is worth while for the U. S. P. to differentiate between the 3 kinds of aloes, Curacao, Socotrine and Cape. The color, size and shape of the three are not characteristic and the fracture does not vary much. The odor from Socotrine aloes is somewhat different from that of the others, being aromatic, or saffron-like on warming while the others give a disagreeable odor. The test is not infallible for the fresh Socotrine does not always give the saffron-like odor. The taste of all varieties is very bitter. The color of the powder is not characteristic even when viewed with the microscope. Two specimens of S. gave 40.7 and 58.6% sol. in cold H₂O. Eleven samples of Barbadoes and Curacao gave from 49 to 76% sol., and 5 samples of Cape from 38.5 to 77.4%. All varieties are almost completely sol. in alc. The color of the H₂O soln. was observed by shaking 1 g. with 25 cc. of H₂O, filtering and making up to 100 cc. in a volumetric flask with H₂O. The color was observed by transmitted white light through the bulk of the flask. The 3 specimens of Socotrine aloes gave a dark yellow soln. The color of the 11 samples of Curacao varied from a dark yellow-orange to a dark red-orange. Of the 4 specimens of Cape 2 were yellow and 2 dark yellow. The HNO₃ color test of the U. S. P. was improved by adding acid to the H₂O soln. prepd. as above in the proportion of 5 of soln. to 3 of HNO₃. The 2 specimens of Socotrine gave a bright yellow color which became a bright red on heating. The Curacao gave a bright red color. The 4 specimens of Cape gave a reddish color which soon became green. All of the specimens conformed to the U. S. P. test for emodin.

L. E. WARREN

The histology of *Viola hark.* FANCHON HART. *J. Am. Pharm. Assoc.* 11, 906-9

(1922).—*Piptadenia macrocarpa* Benthams is the source of Vilca. The bark contains tannin, CaC_2O_4 and resin. Drawings are given. I. E. WARREN

The estimation of gaduol in tasteless extracts of cod liver oil. J. C. KRANTZ, JR. *J. Am. Pharm. Assoc.* 11, 1018-9(1922).—Gaduol is not very sol. in Et_2O or in CHCl_3 but is sol. in EtOH . Consequently its sepn. from aq. liquids is difficult. E. finds that it may be sepd. by satg. the liquid with NaCl and shaking with EtOH . The solvent is evapd. and the residue dried and weighed. A 2% known soln. gave 2.03, 2.13, 2.14 and 2.10%.

I. E. WARREN

MASCARELLI, L. Lezioni di chimica farmaceutica e tossicologica. Parte organica. Torino: Libreria Editrice Giovanni Castellatti. Reviewed in *Giorn. chim. applicata* 4, 182(1922).

PLATZ, HUGO. Über Kapillaranalyse und ihre Anwendung im pharmazeutischen Laboratorium. Leipzig: Willmar Schwabe.

SCHMITZ, HANS. Antimon in der neuen Medizin. Leipzig: J. A. Barth. 68 pp. M 30. Reviewed in *Pharm. Weekblad* 59, 593(1922).

Benzyl acetylsalicylate. A. S. BURDICK and E. B. VLIET. U. S. 1,436,304, Nov. 21. Benzyl acetylsalicylate, a white solid m. $25.5-26^\circ$, sol. in CCl_4 , C_6H_6 , xylene, EtOAc and acetone, only slightly sol. in petroleum ether; it is an antispasmodic; is prepd. by reaction of benzyl salicylate with Ac_2O and NaOAc at 140° for 2 hrs. and distn. *in vacuo*.

Synthetic apple oil. F. B. POWER and V. K. CHESTNUT. U. S. 1,436,290, Nov. 21. A synthetic apple oil is formed of isoamyl esters of formic, acetic, caproic and caprylic acids, AcH , geraniol, geranyl formate and geranyl acetate. This compn. is dedicated for free use without royalty. Cf. C. A. 15, 1057.

Bleaching tobacco. A. DELLING. U. S. 1,437,095, Nov. 28. Tobacco leaf is first treated with an aq. soln. of H_2O_2 alone and then with a H_2O_2 soln. acidulated with tartaric acid.

18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

The manufacture of acids during the war. T. M. LOWRY. *Nature* 110, 777-9 (1922).—A review of the Technical Records of Explosives Supply issued by the (British) Ministry of Munitions and Department of Scientific and Industrial Research.

F. C. Z.

Niter losses in sulfuric acid manufacture. G. ROSENDAHL. *Chem.-Zig.* 46, 1036(1922).—High, unexplained niter losses are more often due to careless workmen on the night shift than to chemical causes. The assumption of Micewicz (cf. C. A. 16, 4015) that high niter losses are caused by As in the Glover tower acid is an error, as many plants make As -rich acids with low niter rates. F or SiF_4 causes high niter losses, probably because these combine with NO and remove it from the field of action. Pyrites cinder dust which gets into the Glover tower also causes high niter losses. It is important, moreover, in order not to obtain losses from improper gas mixts., not to have less than 3 mols. O_2 present for every 2 mols. SO_2 .

F. C. Z.

The Donnan program of investigation for the Chilean nitrate industry. A. W. ALLEN. *Chem. Met. Eng.* 27, 1121-8(1922).—It is by no means evident that the extensive research program proposed by Donnan to investigate the Shanks process is

necessary. Reasons are advanced for discarding the Shanks process entirely, to go to a new method based on extn. at a lower temp. F. C. Z.

Notes on sulfuric acid, sulfur and iron pyrites. CYRIL S. FOX. *Bull. Indian Ind. Labour* 1922, No. 28, 29 pp.—India manufs. about 18,000 tons H_2SO_4 per annum, from imported S. Very little H_2SO_4 is imported. The known S and pyrites deposits are insignificant and hardly worth considering commercially, but there are large and increasing stocks of sulfide Zn ores at the Bawdwin lead mines in Upper Burma, which could serve as a source of S for H_2SO_4 manuf. F. C. Z.

The manufacture of sulfuric acid. L. A. PRATT. *Ind. Eng. Chem.* 15, 11-13 (1923).—A review, based on patents, of progress in the past few years. F. C. Z.

Studies on manganates and permanganates. I. The effect of composition, temperature and moisture on the reactions involved in the manufacture of potassium manganate. H. I. SCHLESINGER. V. T. JACKSON AND E. E. CORDREY. *Ind. Eng. Chem.* 15, 53-7(1923); cf. *C. A.* 13, 1191. F. C. Z.

The treatment of caustic lime sludge. ANON. *Chem. Age* (London) 7, 752-3 (1922).—Caustic lime sludge can be effectively and economically dried by passage through a rotary tube at each end of which a path ring or tire is fixed. Each tire rests upon two or more rollers. Within the tube breakers of elongated steamer-paddle form are placed. When the tube revolves the blades of the breaker "slice" or "hammer" the material being treated. Either internal or external heating is applied. The latter is employed when the products of combustion should not come in contact with the material. W. H. BOYNTON

Fundamental properties of commercial limes. II. The settling of milk of lime suspensions. M. E. HOLMES, G. J. FINK AND F. C. MATHERS. *Chem. Met. Eng.* 27, 1212-16(1922); cf. *C. A.* 16, 3529.—Magnesian limes as a class settle much more rapidly than Ca limes, probably owing to the fact that a higher temp. is necessary in the calcination of Mg limes. The superheated magnesia on slaking is less thoroughly dispersed. As a rule, the higher the available lime content, the slower is the settling, though there were exceptions found. Among Ca limes freshly slaked materials settle more slowly than mechanically hydrated limes, since the latter may contain oxyhydrate. The differences between the settling rates of hydrated limes are less than for freshly slaked limes. Excess water seems to bring out the individual characteristics of the limes; extreme conditions of settling are best obtainable with quicklimes. Freshly slaked Mg limes are more like the corresponding hydrates than are the Ca limes. The lower the temp. of slaking the slower the settling. Sugar decreases the rate; $CaCl_2$ increases it. Soaking of the mechanically hydrated lime decreases the rate of settling. It is possible to obtain limes of almost any settling characteristic, which may be altered by suitable treatment. M. O. LAMAR

The sulfur industry of the U. S. A. G. WOLF. *Can. Mining J.* 43, 856-9(1922).—A general survey, with history of development. A. BUTTS

Use of hydrogen peroxide in the laboratory. F. UTZ. *Südwest. Apoth.-Ztg.* 62, 447-452(1922).—A review of the commercial preps. of H_2O_2 and their uses in the chem. lab. A. G. DU MEZ

Sulfuric acid recovery in oil refineries (SKINNER) 22.

EUCKEN, WALTER. *Die Stickstoffversorgung der Welt*. Stuttgart and Berlin: Deutsche Verlags-Anstalt. Reviewed in *Giorn. chim. ind. applicata* 4, 183(1922).

PARTINGTON, J. R. and PARKER, L. H. *The Nitrogen Industry*. London: Constable & Co., Ltd. 336 pp. 21s. Reviewed in *Chem. News* 125, 286; *Chem. Trade J.* 71, 482(1922); *Engineering* 114, 656(1922).

Synthetic ammonia. F. W. DE JAHN. U. S. 1,436,949, Nov. 28. H and N for NH_3 synthesis are passed over Na amide under high pressure before being brought into contact with the conversion catalyst, to remove traces of injurious associated substances.

Separating salts from mixtures. H. P. BASSETT. U. S. 1,436,228, Nov. 21. Mixts. of NaCl and Na_2SO_4 are treated with a satd. soln. of NaCl at the b.p. to exert a selective solvent action on the Na_2SO_4 . Saline mixts. also contg. Na_2CO_3 may be similarly treated.

Sodium sulfate. N. A. LAURY. U. S. 1,435,930, Nov. 21. For producing Na_2SO_4 from niter cake and NaCl, a rotary furnace is employed the front portion of which has a metal lining and contains balls so that it operates as a ball mill and the rear portion of which has a refractory lining. The reacting materials are fed to the front portion and gradually conveyed to the rear portion of the furnace, which is inclined and heated interiorly.

Cyanamide from calcium cyanamide. J. H. LINCOLN. U. S. 1,436,179, Nov. 21. Ca cyanamide is gradually added to an aq. soln. simultaneously with CO_2 so as to maintain the alkalinity of the soln. during the reaction below 0.5 N. A concd. soln. nearly free from dicyanodiamide is thus obtained.

Separating magnesia from calcined dolomite. R. A. W. BLACK. U. S. 1,436,230, Nov. 21. Calcined dolomite is treated with H_2O which has been previously satd. with lime and treated with CO_2 to remove slightly less than 100% of the $\text{Ca}(\text{OH})_2$, leaving the soln. slightly alk., in order to dissolve $\text{Ca}(\text{OH})_2$ and leave magnesia. The soln. is regenerated with CO_2 for further use.

Oxides of iron and sulfur from ferrous sulfate. H. B. KIPPER. U. S. 1,435,928, Nov. 21. In heating FeSO_4 to above 400° to form Fe_2O_3 and S oxides, the material is subjected to a grinding and mixing action to facilitate the reaction during its progress. The operation may for this purpose be carried out in a ball mill.

Handling nickel carbonyl. R. LESSING. U. S. 1,436,662, Nov. 28. In the use of Ni carbonyl in hydrogenating org. compds. or other processes, the Ni carbonyl is stored in an absorbent material such as charcoal or coke impregnated with oil and then when desired for use is taken up by passing H, N or other gas into contact with the absorbed supply in storage.

Tung oil composition for use in impregnating fiber. W. R. SEIGLE. U. S. 1,436,362, Nov. 21. Tung oil is partially hydrogenated, gilsonite is dissolved in the oil and the mixt. is then heated to effect polymerization and render the product suitable for use with fiber in the manuf. of brake linings or other articles.

Clutch facing composition. W. C. FISHER. U. S. 1,436,158, Nov. 21. A hardened compn. is formed from asbestos, cork, a resinous condensation product and rosin.

Fireproofed pyroxylin-coated fabric. G. BLENIO. U. S. 1,436,231, Nov. 21. Fabric adapted for making airplane wings or automobile tops is successively impregnated with NH_3 , phosphate and a pyroxylin varnish and then coated with a film of pyroxylin contg. MgCl_2 or other fireproofing agent.

Fire-extinguishing material. J. B. ELLERY and A. DRUMTRA. U. S. 1,435,957, Nov. 21. Granulated cork coated with Na silicate.

Filler for celluloid articles. H. SCHNIGER. U. S. 1,436,203, Nov. 21. A hard but non-brittle compn. adapted for filling hollow celluloid brush backs or similar articles is formed from rosin 15, paraffin wax 20 and marble dust or terra alba 20 parts.

Aqueous solution of low freezing point. C. V. STRINHART. U. S. 1,436,828, Nov. 28. A soln. adapted for use in automobile radiators is formed of CaCl_2 , borax, glycerol and H_2O .

Furnace for burning sulfur. A. HANSEN. U. S. 1,436,762, Nov. 28. The S

combustion chamber contains rotatable parallel disks mounted on a central shaft extending horizontally and carrying ribs parallel to the shaft on their peripheries.

Furnace for calcining hydromagnesite. C. E. OLIVER. U. S. 1,436,520, Nov. 21. The material to be calcined is placed on a platform moving in a direction opposite to that of furnace gases which pass over it.

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

Porcelain making and the electrical industry. ANON. *Electrician*, 89, 690 (1923).—2 illus. Brief description of the Havelock Pottery Works. C. G. P.

A new refractory material. W. SMITH. *J. West Scotland Iron and Steel Inst.* 30, 8-13 (1922).—The new refractory is *carbonized clay*. Mixts. of C and clay are old but carbonizing by C-charged gases has never been well developed. Charging is done when the clay is in the biscuit state and at max. porosity. Shrinkage, with higher burning, then compresses the C to a d. comparable to that of steel. So long as carbonized clay remains in a reducing atm. it will withstand the highest com. temps. and is unaffected by acids. Much skill is required in the carbonizing process. Ground raw clay and coal are heated together in a muffle kiln. The evolved gases may be used for fuel and coke is obtained. Pitch may be used as a binder in forming shapes of carbonized clay. There is no after-contraction. White carbonized clay is made by burning out the C in carbonized clay. The black is suitable for heat resistance in a reducing atm., for acid-resisting ware and for abrasives. The white is suitable for heat resistance in an oxidizing atm. Carbonization may be a means of extracting Fe and alkalis from clays. The reports are based upon lab. tests. Com. tests will be made. C. H. KERR

SPRINGER, L. *Überwachung des Feuerungsbetriebes in der Glas-Email und Tonindustrie.* Berlin: Keramische Rundschau.

20—CEMENT AND OTHER BUILDING MATERIALS

C. N. WILEY

Aluminous cement. BIED. *Rev. univ. mines* July 1922; *Technique moderne* 14, 508-9 (1922).—Aluminous cements are cements with a high Al_2O_3 content, known commercially as "fused," "elec.," or "electro-fused" cement, in which the Al_2O_3 content is equal to or greater than the SiO_2 content. They are produced by fusion because Ca aluminates do not soften and clinkering is very difficult. Methods of manuf. are described. The compn. is about: SiO_2 10-12, Al_2O_3 40-45, CaO 35-40, FeO 15-20%. Setting starts in about 4 hrs., and is complete in 7-8 hrs. Hardening is very rapid and an ordinary concrete (800 l. gravel, 400 l. sand, 350 kg. cement) has a min. strength of 300 kg. per cm.² in 72 hrs., which is much higher than the strength of Portland cements after 90 days. Also in *Rev. metal.* 19, 759-64 (1922). A. P.-C.

ECKEL, EDWIN C. *Cements, Limes, and Plasters.* 2nd ed. Revised and enlarged. New York: John Wiley & Sons. \$6.50. Reviewed in *Eng. Mining J.-Press.* 114, 1126 (1922).

Strengthening composition for cement mixtures. A. T. MALMED. *J. S.* 1,436,276,

Nov. 21. A mixt. of diatomaceous earth and CaCl_2 or similar materials is used for strengthening port. cement concretes and mortars.

Magnesia plaster. R. YAMAMOTO. U. S. 1,436,747, Nov. 28. Asbestos or other fibrous material 10, is mixed with MgO 40, pigment 5, powd. peanut shells 5 and a concd. soln. of MgCl_2 44° Bé. dissolved in dil. $\text{Pb}(\text{OAc})_2$ soln. 2 parts, to form a plaster which is rendered relatively non-hygroscopic.

21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

A method of carbonizing low-grade fuels, especially refuse. ERNST WOLFF. *Chem. Ztg.* 46, 1057-9(1922).—Lab. expts. showed that 1 kg. of household refuse, after sorting, would yield 25 l. of a gas contg. CO_2 51.1, illuminants 3.4, CO 8.3, H 7.2, CH_4 24.4, and N 5.6%. The residual coke is just enough to supply the heat for the process, if some of the tar is added. It is powdery and light. The process proceeds between 145° and 500°, the H becoming large above 350°. W. proposes a plant in which the flue gases dry the refuse, and the coke is compressed hot and fed directly to the producer. The rubbish used contained 53% moisture and 28% ash. ERNEST W. THIELE

A national (French) liquid fuel. C. MARILLER. *Technique moderne* 14, 497-9 (1922).—A brief general discussion of the use of alcohol as a motor fuel, both pure and in admixt. with gasoline. A. P.-C.

Testing fuels for high-compression engines. S. M. LEE AND S. W. SPARROW. *J. Soc. Automotive Eng.* 12, 11-16(1923).—For mixts. of C_2H_6 and gasoline in aviation engines the compression ratios and % by vol. of C_2H_6 resp., are given as follows: 5.4, 0; 6.1, 30; 7.2, 65; 9.2, 85; 11.5, 100; 14.0, 100. Alc. was found about twice as effective as C_2H_6 at low compressions in preventing detonation. At higher ratios where less gasoline was used in the fuel, there appeared to be little difference between the effect of alc. and benzene. Preignition depends upon (a) the heat of compression and (b) heat supplied to the charge by local hot spots in the cylinders. The first is increased by an increase in the compression ratio and the second is probably decreased. The change in heat of compression can be calcd. by the relation $T_2 = T_1 r^{n-1}$, where n is 1.25 to 1.40, r is the compression ratio, T_1 abs. temp. at the beginning of the compression and T_2 the abs. temp. at the end of compression. Thus engines may require different fuel blends solely because differences in design give them unequal tendencies to preignition. D. F. BROWN

Pulverized lignite as boiler fuel. ANON. *Engineering* 114, 620(1922).—Boiler tests on South Australian lignite showed that this can be satisfactorily used for steam-raising if burned in a pulverized form after a preliminary drying to reduce the moisture content to 15% or less. This would be effected in rotary kilns heated by the waste flue gases. The exptl. efficiency of boiler and superheater heated by this fuel was 76%, which would have been raised to 85% by using the economizer. J. L. WILEY

The 1922 peat experiments. ANON. *Can. Mining J.* 43, 852-4(1922); cf. C. A. 16, 3191.—A list is given of Canadian peat bogs, with the fuel content and av. heating value for each.—High-quality peat was produced in 1922 with the Anrep-Moore machine at a cost of \$3.50 per ton, and was sold at \$5 per ton for power generation as well as for domestic use. A. BUTTS

The utilization of Alpine anthracite. MOULINIER. *Rev. Métal.* 19, 600-13 (1922).—Alpine anthracite is a graphitic anthracite with an ash content varying from a few % to 30-35%. Its physical characteristics make it very difficult to burn on a fixed grate, especially when quite dry. Washing, both by the usual processes and by

flotation, does not give satisfactory results. The most satisfactory method of burning it is in the pulverized form, for which it is well suited. Results of successful boiler tests carried out in 1920-21 are given. A. P.-C.

The science of industrial heating. C. M. STERN. *Rev. metal.* 19, 579-89(1922).—A general discussion, showing the very considerable contributions of H. LeChatelier to this important branch of science. A. P.-C.

The composition of gaseous fuels in relation to their utilization. W. PAYMAN AND R. V. WHEELER. *Fuel* 124, 185-96(1922).—A study of the effect of varying the % of CH_4 , H, CO, CO_2 and N on the mode of burning of a gaseous fuel in an industrial burner, with especial reference to the industrial gases commonly used. Examples are given to show the usefulness of speed-% curves in adjusting burners or altering the compn. of the gas to procure a max. efficiency and the requisite calorific intensity. The speed-% curves are based upon the "Law of Speeds" (cf. C. A. 14, 1042, 1043, 1221; 16, 1851). Since a very short Bunsen flame will not fill the furnace and a long flame overheats the end and causes loss of heat, and since the length of flame depends upon the compn. of the gas, it is very important to choose the correct compn. of gas to obtain the optimum combination of these factors. The use of CH_4 alone allows a high degree of primary aeration, but only a small range of adjustment. CO alone also allows a high primary aeration without the flame striking back and enables a wide range of adjustment of the primary air. H alone allows very little primary aeration with a resulting flame of low calorific intensity. A speed-% curve can be constructed for any inflammable mixt. of known compn. from the speeds of flame in mixts. of the simple constituents in air. The general effect of mixing CH_4 , H and CO are as follows: (1) Mixing CH_4 with H greatly reduces the max. speed of flame obtainable below that given by H and air alone; (2) though the max. speed of flame in any CO-air mixt. is fairly close to that of any CH_4 -air mixt., the former is less effective in reducing the max. speed obtainable with H-air when it is mixed with them; (3) the addn. of CO to a CH_4 -H mixt. has little effect on the max. speed of flame, but widens the range of inflammability and therefore gives the mixt. greater adaptability in a Bunsen burner. Addn. of H_2O gas to coal gas increases the amt. of gas which must be burned by secondary air, with resulting reduction in the calorific intensity of the flame, but with increase in the margin of adjustment. To obtain greater intensity with increasing % of H_2O -gas, it is necessary to increase the speed of the gas-air current, and when this is practicable, a large % of H_2O -gas is not disadvantageous, and would give greater range of mixts. of such gas with air. Incombustible gases have little effect on the max. speed of flame, even when as high as 30%. The calorific value is also little affected by such addns. The inferiority actually found in dild. coal gas can be explained by the steepness of the right-hand slope of the speed-% curve. Increase in N increases the steepness, meaning that the margin of adjustment between the max.-speed mixt. and the upper limit mixt. decreases with increase in N. A small range of adjustment means that slight variations in pressure cause wide fluctuations in the flame and the heat distribution throughout it, with consequent inefficiency in the furnace. A very small change in compn. with 30% N changes a short finly aerated flame to a long luminous one. A high % of N or CO_2 is to be avoided with burners of the Bunsen type. The margin of adjustment for town gas with H_2O -gas added is greater than for coal gas, so the addn. of N or CO_2 has a less pronounced effect. But such addn. gives too low a calorific value for town use. Producer gas, regarded as a H_2O -gas-N mixt., is reliable even if contg. 50% N.

C. C. DAVIS

Powdered coal as fuel in steam plants. H. KREISINGER AND J. BLIZARD. *Proc. Eng. Soc. Western Penn.* 38, 169-200(1922).—Three groups of tests using powd. coal on a 3-pass Edge Moor boiler equipped with a "Loptico" furnace and the results of a

9-day test on 2 Stirling boilers are reported. Overall thermal efficiencies of from 80% to over 90% were obtained. Drawings of furnace settings, the burner for powd. coal, the isothermal lines in operation of a furnace burning powd. coal, together with graphs showing the % CO_2 , excess air, temp. of flue gas and uniformity of furnace conditions with variable load are given. Prevention of the destruction of furnace lining by high temp., easy removal of ash, effect of a water screen in the furnace and recent improvements in furnace design are discussed. Much valuable information comparing stoker fired furnaces with those burning powd. coal is contained in the extended discussion which follows the article.

W. W. HONG

Banded bituminous coal. A. BARANOV AND W. FRANCIS. *Fuel* **124**, 219-22 (1922).—Certain writers have inaccurately based generalizations about the constituents of banded bituminous coal on data reported on only 1 coal (cf. *C. A.* **13**, 1755, 2585; **14**, 1888, 1889). Data on the vitrain (A), clarain (B), durain (C) and fusain (D) of a Nottinghamshire banded coal are given. Comparison of the results with previous ones showed that in general the A of all the banded coals contd. the highest % H_2O and the lowest % ash. Approx. 10% by wt. of the coals consisted of A, corresponding to 5% of the seam. No pure B could be sepd., but intimate mixts. of B with A and with C occurred. Approx. 12% B and 75% C was estd. in the coal. D was in soft flaky fibrous deposits and was approx. 3% of the seam. HNO_3 -HF mixt. dissolved all A to a clear dark brown soln., B to a lighter soln. contg. transparent solid fragments of cuticles and spore exines, and approx. 0.5 the C to a yellow soln. contg. opaque spore exines. The acids did not attack the D. A formed a porous, swollen coke, B a strong dense one not much swollen and C and D a non-coherent mass. A mixt. of 1 part A and 4 C gave at 900° a coke similar in quality and character to that from B. The ash of A was deep red-brown, contg. much CaSO_4 , MgO and alkalis, of B reddish with much CaSO_4 , Al_2O_3 and SiO_2 , of C gray-white chiefly Al_2O_3 and SiO_2 , with no alkalis and of D brown-gray with much Ca and Al silicates. Those of A and B were light and feathery. The presence of large amts. of Ca salts in the D ash is due to the absorption of H_2O contg. Ca. The white flakes in the cleats of the seam were nearly pure CaCO_3 .

C. C. DAVIS

Examining coal in incident light. ALFRED GRADENWITZ. *Coal Age* **22**, 957-8 (1922).—The metallographical method of investigation in incident light shows that every solid fuel possesses throughout a characteristic structure. In peat, lignite and true coal remarkable meshy tissues of round micro-cells were noted, affording a valuable clue to the genesis of coal. The conclusion is made that all kinds of coal, glance coal as well as dull coal, should be considered as solid colloidal matter. Glance coals are shown to be wood products, the longitudinal fibers and tissue bundles coming out most clearly after etching. Four photomicrographs are shown.

J. L. WILEY

Controlled flameless firing, without an explosive mixture. ANON. *Gas J.* **160**, 733-4 (1922).—Operating data are given of "Captive Fire," a system of firing for annealing and metal-melting furnaces whereby a const. mixt. of air and gaseous fuel is assured, whatever the variations of inlet pressure on the one hand, and consumption on the other. The fuel economy over that of coke-fired furnaces varied from 25 to 50%.

J. L. WILEY

The action of solvents on coal. S. ROY ILLINGWORTH. *Fuel* **124**, 213-9 (1922).—The action of solvents on coal and the best means for resolving it into β - and γ -compsds. were studied. To this end, the nature of the solvent and of the coal, and the temp. of extn. were investigated for their comparative influence. All samples were freshly mined, 120-mesh, and dried *in vacuo* at 105°. The app. used for all extns. is described and illustrated. In general, it was found that the action of various solvents was due to a depolymerization of the coal substance. The higher the C/H ratio the greater

the degree of polymerization, and consequently the less readily were coals of high C/H ratio resolved into their components, and coals with C/H of over 20 were in general so highly polymerized that the action of solvents was very slow or nil. Coals with C/H over 21 were practically unattacked by pyridine (A) at 180°. The effect of increase in temp. was most marked for coals with C/H 17–20. The smaller effect in coals of lower C/H was due to the fact that A-sol. compds. were so slightly polymerized that they were depolymerized at the temp. of the Soxhlet extn. and became sol. The increase in amt. of sol. compds. by A extn. subsequent to heating the coal dry, was dependent on the nature of the coal, the temp., and time of heating. With C/H below 17, there was no marked increase in final ext. but the rate of extn. increased greatly. For each coal was found a min. temp. below which complete depolymerization of the ultimately sol. complex did not occur. This min. temp. increased with increase in C/H. With phenol (B), rapid soln. occurred at first, with a subsequent marked decrease in the rate. The γ compd. was more readily extd. than the β , and those components which were least easy to dissolve were those of high C/H ratio. A comparison of A, B and aniline showed that at 100° A exerted the greatest effect, but its action at higher temps. was much less than that of the others. B at its b. p. had the greatest depolymerizing action. The difference in depolymerizing power was not due to differing solvent power for there was always sufficient solvent to dissolve all compds. in a condition to be dissolved, and all depolymerized compds. were equally sol. in each solvent. Since B not only had the greatest depolymerizing action but was easiest to manipulate it is recommended as the most suitable solvent.

C. C. DAVIS

Comparative steaming tests of Nenana lignite and Matanuska bituminous coals. J. A. DAVIS AND P. HOPKINS. Bur. of Mines, *Repts. Investigations* No. 2412, 9 pp. (1922).—Comparative results are given of 15-hr. tests carried out at the Anchorage power plant of the Alaskan Engineering Commission.

C. T. WHITE

Experiments on coal dust and the combustion of pulverized coal. ARNOUD DE GREY. *Rev. métal.* 19, 645–55 (1922).—From the results of extensive tests carried out by Tafanel on the ignition of coal dust from 1907–14 at the expt. gallery of Liévin and in 1913 in a mine gallery at Commentry, and by E. Audibert since 1921 at the Montluçon expt. station, DeG. works out the proper design of burners for pulverized coals, the velocity with which the coal should travel in the burner and on leaving the nozzle, the dimensions and shape of the combustion chamber, and the possibility of using various grades of fuels and especially low-grade fuels (showing the possibility of mixing them with poor gas).

A. P.-C.

Proposed simple alternative method of testing mine dusts. J. W. WHITAKER. *Iron Coal Trades Rev.* 105, 886–7 (1922).—Detn. of the combustible matter in mine dusts by a sp. gr. method employing the stone-dust meter is compared with the usual method of incineration. The former method is more efficient in connection with stone-dusting of coal mines, especially where gypsum or carbonate-stone dusts are used. Data of tests are given.

J. L. WILEY

Some recent developments of powdered-coal firing. J. S. ATRINSON. *Iron Coal Trades Rev.* 105, 924–7 (1922).—The prepn. and utilization of powdered coal are discussed in connection with its drying, pulverizing, burning, and the removal of the ash. The turbo-pulverizer is especially recommended (cf. C. A. 16, 1001). Under usual working conditions an efficiency on boiler, superheater and economizer of 88% can be obtained and maintained with pulverized coal.

J. L. WILEY

Gasification of Ohio coals. D. J. DEMOREST. *Chem. Met. Eng.* 27, 1172–5, 1221–4 (1922).—The suitability of Ohio coals for gas manuf. was studied in a vertical retort of commercial size. The methods of operation of the retort and various methods of control analyses are also given. The data are tabulated and discussed.

Coke suitable for domestic heating but inferior for metallurgy was obtained. A little less tar and about the same amts. of NH_3 were produced as from standard gas coal. About the same vol. of gas as from standard gas coal but with lower calorific value was obtained.

W. A. MUELLER

Scrubbing and condensing coal gas. J. R. WOHRLEY. *Gas Age-Record* 50, 521-6, 530; *Am. Gas J.* 117, 494-8(1922).—The Doherty-Washer Cooler is explained in connection with a discussion of the proper methods and facilities to be used and their effect upon NH_3 recovery in a coal gas plant. (Cf. Steere, C. A. 16, 4328.) This app. combines the condensing, scrubbing, extrn. of tar, and removal of NH_3 in a single shell or a series of shells. Furthermore, it reduces the H_2S content about 20%. The advantages of this app. are given and an NH_3 balance is given.

J. L. WILEY

Determination of benzene in coal gas. A. THAU. *Chem. Age* (London) 7, 636-8 (1922).—The Bertbold absorption bottle is described with illustrations. It is rather complex in construction, but is simple to handle and efficient in operation. The most satisfactory absorbing medium is odorless and water-white medicinal petroleum oil, b. 330° , d. about 0.8863, precipd. according to the specification of the German pharmacopeia. In applying the bottle to the benzene test it is weighed and connected on one side to a wash bottle contg. a satd. soln. of picric acid for naphthalene removal and 3 CaCl_2 U-tubes, and on the other side to a gas meter provided with thermometer and pressure gage, and an exhaustor. The CaCl_2 tubes and the absorption bottle are surrounded by a freezing mixt. For a test 300-400 l. of gas are passed through the app. at a rate not exceeding 50 l. per hr. By means of the freezing mixt. the gas and oil are cooled to -15 to -20° so that the vapor pressure of the benzene is reduced considerably. After the washing is completed, the bottle is wiped clean, the gas contained in the upper part of the bottle is displaced by air, and after having reached room temp., the bottle is weighed again, the increase in wt. representing the amt. of benzene hydrocarbons contained in the gas.

J. L. WILEY

Complete gasification and the Tully plant. N. S. SMITH. *Gas J.* 160, 736-8, 800-1 (1922).—The development of the Tully gas-producer plant is traced, and operating data from a 300,000-cu. ft. per-day plant at Ossett are given. 100% coke, 20% coal and 80% coke, 50% each of coal and coke, and 100% coal were used in each of 4 tests. The results were resp. as follows: gas make per ton 48250, 45000, 54000, 53500 cu. ft., calorific value 290, 305, 316, 333 B.t.u. per cu. ft., about $\frac{1}{4}$ being coal gas the rest water gas; thermal efficiency of gas production 40.5, 39.4, 45.6, 43.2; cost per 1000 cu. ft. 8.65, 9.10, 7.35, 6.84 d.

J. L. WILEY

The production of town's gas by fractionation of coke-oven gas. H. THYSSSEN. *Rev. universelle mines* 10, 506-12(1921); *Fuel* 124, 223.—Coke ovens are operated primarily for the production of good coke. Nevertheless chamber ovens have advantages in working and first cost over gas retorts. It is urged that a gas suitable for lighting be obtained by fractionation of the gas formed in coking a coal for metallurgical coke. The gas rich in hydrocarbons produced in the earlier stages and that poorer in hydrocarbons produced later should receive sep. treatment. The poor gas is burned under the ovens, the deficiency in heating power being made up by addn. of independently made producer- or water-gas. The process has been applied in many installations in the Rhine and Ruhr regions.

C. C. DAVIS

Rational substitution of manufactured gas and coke for natural gas and anthracite in Buffalo, New York. Geo. S. BREWER. *Am. Gas Assoc. Monthly* 4, 693-8(1922).—In cities such as Buffalo, using natural gas and anthracite, the supplies of each of which are being depleted, the problem of obtaining sufficient fuel supplies resolves itself into the gradual substitution of coke or anthracite for domestic heating purposes, and the gradual change from natural gas to mixts. of this with coal gas and blue water gas

to the extent that legal heating standards will not be disturbed and the sp. gr. of the gas will be maintained within narrow limits. The most desirable type of coal-gas plant will probably be coke ovens or vertical retorts. In order to det. the relative vols. of the 3 gases, charts have been prepared and formulas evolved, based upon chem. analysis of these gases and the math. relation between their heating values and sp. gr., which show the % of the gases by vol., the heating value of the mixed gas, and the sp. gr. of any desired mixt.

J. L. WILEY

Industrial gas firing by the surface-combustion process. H. LININGER. *Z. Ver. Gas-Wasserfach.* 62, 55-62(1922).—The furnaces described are American. The gas pressure is kept at atm., and a specially designed burner causes the air stream to draw in the theoretical amt. of gas at all loads, and insures thorough mixing. The mixt., entering with high velocity, is retarded and burned on any refractory packing of proper size. The vol. of the flame is small; hence with city gas a temp. within 150° of the theoretical can be attained. With producer gas 1270° can be reached against 1380° theoretical. The high temps. make for high efficiency also.

E. W. T.

The production of carbon-black from natural gas by the high-voltage arc. J. J. JAKOWSKY. *Bur. Mines, Repts. Investigations* No. 2417, 10 pp.(1922).—The use of a magnetically spread arc is not successful; the intermittent type and the continuous type of app. show some promise. The C-black recovery per unit vol. of gas varies with the current, the rate of gas flow, and the type of app. With the intermittent type the max. yield of C per kw.-hr. input is obtained with 6 amp. flowing in the primary circuit and an input of 41 kw.-hr./lb. of C recovered. When water is used as wash soln. in the continuous process, the yield per kw.-hr. is less than when oil is used. The presence of larger quantities of CO and CO₂ indicates reaction between the hydrocarbons and the dissociated water vapor. High-frequency expts. indicate that the decompu. of natural gas by a high-voltage arc is not purely a heat reaction. Different types of app. are illus. and rates of flow shown by curves.

W. H. BOYNTON

Conditions affecting the activity of iron oxide in gas purification. W. A. DUNKLEY AND R. D. LEBTCH. *Am. Gas Assoc. Monthly* 4, 699-704(1922); cf. *C. A.* 15, 2799.—A study was made of the activity of oxides chiefly when in the fresh condition. The measure of activity adopted was taken as the max. rate at which the gas contg. H₂S in dilns. comparable with purification practice could be passed through a specified wt. (1 g.) of oxide packed in a tube under prescribed conditions, with complete removal of the H₂S from the gas. The app. employed was that designed by Fieldner, Powell and Scott of the Bur. of Mines and slightly modified by the authors. (Details and fig. are given.) Several types of oxides were used in the tests. Different oxides are affected differently by variations in water content. With each oxide there is a most favorable content; variations from this decrease the activity. The activity seems to be a matter of surface. For action the surface must be moist but if too wet the H₂S is excluded in a measure and the activity decreases. All the oxides tested showed the same temp. effect on activity; this increased from 45° up to about 115° or 120°, after which there was an appreciable decrease. The total increase up to the max. was approx. 10%. The effect of different concns. of H₂S from 10 to 1000 grains per 100 cu. ft. upon oxide activity was studied. All of the oxides showed nearly the same activity with 10 grains and this activity was higher than with higher concns. In general the material of lower oxide content suffered less decrease in activity with the higher concns. than did those very high in Fe. In most cases there was very little decrease after a concn. of 500-600 grains was reached. The action of different types of oxides was widely different depending upon the degree of sulfiding from 0 to 85% of the theoretical. Some of those initially most active dropped off in activity very rapidly when partly fouled. A rusted Fe-borings oxide was most conspicuous in its power to maintain a moderately high

activity over a wide range of sulfiding. Expts. with oxides treated with various amts. of acids or alkalis do not indicate that these have any marked effect upon the activity of fresh materials. J. L. WILEY

Production of by-product producer gas under low-temperature conditions. N. E. RAMBUSH. *Iron Coal Trades Rev.* 105, 917-19(1922).—To obtain a high yield of by-products economically, it is essential, so far as the tar is concerned, that the fuel be submitted to a low-temp. treatment, while in the case of NH_3 there should be a long time-factor between the steam and the C in the fuel. Both these conditions are obtained by observing only one, since as soon as a long time-factor is given, then more steam is decomposed, and the final temp. of the gas leaving the fuel is decreased. The fuel at its entrance to the producer should not be submitted to a temp. above 300-400° if cracking of the tars is to be avoided. Also for the same load the lower the gas-outlet temp. the higher will be the heating value of the gas. The only practical way in which to obtain the longer gasification period together with a low gas-outlet temp. is to increase the fuel depth of the producer instead of reducing the gasification rate per unit of cross-sectional area of the producer. Apart from the advantages attached to a low-temp. type of producer of increased thermal efficiency and gas quality, as well as higher NH_3 and tar yield, and a more greatly reduced steam consumption, there are the further advantages that the gas quality remains steady independently of the charging intervals, and with a deep-fuel bed the producer can easily carry overload without increased operating difficulties. Embodying these principles are the "Semi-low-temp." and the "True-low-temp." types of by-product gas producers developed by the Power Gas Corp. (cf. C. A. 16, 2209) as modifications of the Mond producer. Comparative operating data of the 3 types are given. A general improvement in results is noted. The app. is covered by Eng. patent 188,607 (*Gas J.* 161, 38). Also in *J. West Scotland Iron Steel Inst.* 30, 18-32(1923). J. L. WILEY

The Stein-Chapman gas producer with mechanical agitator. ANON. *Engineering* 114, 597-8(1922); 8 figs.—The mech. construction of 3 special features of the producer are described: the automatic feed, the mech. floating agitator, and the automatic, continuous ash remover. J. L. WILEY

Gasification of crude lignite containing considerable water. G. H. MEYER. *Am. Gas J.* 117, 711-14(1922).—Translation (cf. C. A. 16, 4044). J. L. WILEY

Water gas. A. PARKER. *Gas J.* 161, 27-33(1923).—An excellent exposition of water-gas plant operation (cf. C. A. 15, 2709; 16, 2771). J. L. WILEY

Fused-ash gas producers. A. FOLLET. *Chimie et industrie* 8, 965-73(1922).—A review. A. P.-C.

The use of pulverized coal for heating boilers and furnaces in general. PAUL FRION. *Chimie et industrie* 8, 736-57, 974-88(1922).—An excellent review. A. P.-C.

The combustion of bituminous shales in gas producers. N. N. DOBROKHOROV. *Industrie russe petrole schistes* No. 5-8, 259-69 (Aug. 1921); *Rev. métal.* 19, 532-3 (Abs.) (1922).—It is essential to obtain a gas contg. as little tar as possible, either by using a producer with two combustion zones, or by intensifying the gasification so as to decrease the time during which the fuel is in the producer. The latter is preferable with bituminous shales. In a producer with dry blast a suitable time would be 3-4 hrs. As the ash is high in CaO and in Al_2O_3 (especially in the Baltic provinces), it acts like a hydraulic lime, so that water seals cannot be used. The heat balance is given and a description of a proposed form of producer. If the cost per cal. of a shale is less than that of another fuel, the use of the shale is advantageous, the disadvantage due to the excess of ash being offset by the possibility of using the latter in the place of hydraulic lime. A. P.-C.

The use of hot-blast, fused-ash gas producers. AUGUSTE DESSEMOND. *Rev. métal.* 19, 656-64(1922).—The merits of this type of producer are: ease of operation,

reliability, great flexibility, adaptability to any fuel (0-40% volatile, 10-70% ash), small space occupied for large capacity, small amt. of labor required, suitability of the gases for use (after thorough purification) in gas engines or (after slight purification) under boilers, recovery of by-products of low-temp. carbonization. The efficiencies obtained with various grades of fuel when burned in ordinary furnaces and in hot-blast fused-ash producers are compared. With low-ash fuels, by suitable additions of materials, the slag drawn off can be used directly as a cement (generally as an aluminous cement) of excellent quality; and with high-ash fuels the slags can be mixed with Portland cement, hydraulic lime, etc., to make cements equal to and better than the best blast-furnace slag cements. A. P.-C.

Relative usefulness of gases of different heating value and adjustments of burners for changes in heating value and specific gravity. W. M. BERRY, I. V. BRUMBAUGH, J. H. EISEMAN, G. F. MOULTON AND G. B. SHAWN. *Bur. Standards, Tech. Papers* 222, 91 pp.(1922).—Results of an extensive series of lab. tests carried out by the Bur. of Standards are given. These tests were made in connection with an investigation carried out by the Public Service Commission of Maryland to det. the most economic heating value standard for manufd. gas in the city of Baltimore. C. T. WHITE

Gas meters: Their construction and application. A. T. GILBERT. *Gas J.* 160, 622-4(1922). J. L. WILEY

The "Electro" flow meter. JOHN TERRACE. *Gas J.* 160, 619-22(1922); 6 figs.—A description is given of an elec. flow meter applied to the measurement of gas in the mains. Comparative tests with a station meter show very close agreement; over 2 months the difference was only 0.81%. J. L. WILEY

The supply of power at collieries. F. S. ATKINSON. *Fuel* 124, 211-3(1922).—Collieries connected with by-product coke ovens have usually a surplus of gas over that for heating the oven flues. The surplus should be used for town supply or to generate power. But it has been found that it is best to take advantage of an available market by erecting by-product gas producing plants to supply the ovens with low-grade producer gas. The higher-grade coke-oven gas is thus released for town use. Power can be provided from surplus coke-oven gas either in large gas engines, or for steam boilers. C. C. DAVIS

New combination by-product coke oven. JOS. BECKER. *Iron Age* 110, 1275-9 (1922); cf. C. A. 16, 4331.—Construction and operation of Koppers Co. new combination oven A are described. The new feature of this oven is that the burnt gases from the vertical heating flues on one end of the oven pass over across the top of the oven and down the vertical flues on the same end of the oven. This permits deeper ovens, more even heating, shorter coking time and greater oven capacity. It simplifies oven construction, gives greater wall strength and lower fuel consumption; it avoids counter flow between flame flues and gas supply flues and gas regenerators. A comparison between American and European coking practice is made with the claim that the former is superior. J. J. MORGAN

By-product coking with particular reference to new combination oven. JOSEPH BECKER. *Blast Furnace Steel Plant* 10, 575-83(1922); cf. C. A. 16, 4331 and preceding abstract. J. J. MORGAN

Foundry coke (YOUNG) 9. Moorlands brown-coal deposits (BROUGHTON) 8.

Extracting coal and separating hydrocarbons. H. PLAUSON. U. S. 1,436,289, Nov. 21. A mixt. of SO₂ with a ketone is used for extg. coal or for sepg. satd. from unsatd. hydrocarbons. Acetone and SO₂ ext. from anthracite 1% of a dark red sub-

stance, which yields on fractionation an oily hydrocarbon. Extn. under 70 atm. pressure increases the yield to 4.8%. A resinous or wax-like product (20-3%) is obtained from lignite by extn. under pressure. By pretreating the material with alc. or aq. NaOH under pressure, larger yields are obtained by the SO₂-acetone extn. Crude naphtha may be treated with SO₂ and acetone at 0-15° to sep. satd. and unsatd. hydrocarbons. Diolefins can be sepd. from gases by the SO₂-ketone mixt. C₃H₂ is but slightly sol. in the SO₂-acetone mixt. (satd. with SO₂). In some instances a cryst. compd. contg. acetone and diolefin-SO₂ compd. may be formed from the extn. products.

Self-sealing tank for liquid fuels. E. FRIANT. U. S. 1,436,985, Nov. 28. Metal tanks for holding gasoline, etc., are surrounded by viscous material and fibrous packing encased in rubber to render them self-sealing when punctured.

Apparatus for distilling shale, coal, wood or other carbonaceous materials. E. D. DEETER. U. S. 1,437,292, Nov. 28. An inclined rotatable feeding tube delivers material to be treated to a retort through a vapor-tight connection.

Fabrics for gas mantles. J. T. ROMIN. U. S. 1,436,359, Nov. 21. See Brit. 169,277 (C. A. 16, 824).

Incandescent gas mantles. J. P. H. SOPER and T. TERRELL, JR. U. S. 1,436,296, Nov. 21. Fabric for mantles is impregnated with a soln. of Th and Ce nitrates or other illuminating salts, dried, treated with an alk. soln. of NaF or KF and then washed and dried. The fluoride serves to ppt. Th and Ce fluorides in the fabric.

Purifying coke-oven gas. C. J. RAMSBURG. U. S. 1,436,196, Nov. 21. S is removed from the gas by action of an alkali soln., e. g., Na₂CO₃, and the soln. contg. impurities thus removed is brought into contact with hydrated Fe oxide to form Fe sulfide and regenerate the soln. for further use. The Fe sulfide is subjected to aeration to drive off the S and regenerate Fe oxide.

Horizontal coke ovens with vertical heating flues. W. HIBY. U. S. 1,436,004-5-6-7-8, Nov. 21.

22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Properties of crude oils. J. B. RATHBUN. *Petroleum Age* 10, No. 12, 37-9 (1922).—Compilation of data on Russian, and East Indies crude oils showing principal fields, location, history, % of production, analysis and phys. data of the oils from each field.

D. F. BROWN

Properties of crude oils. J. B. RATHBUN. *Petroleum Age* 11, No. 1, 39 (1923).—Properties of Penna. crudes with distn. data at ordinary pressures and at 40 mm. are given, also properties of crudes from Argentina, Chile, Brazil and Peru together with a list of the principal producing fields and their locations.

D. F. BROWN

Production and field data of the Gulf Coastal, Texas, crudes. P. WAGNER. *Nat. Petroleum News* 14, No. 52, 35-9 (1922).—Analytical and distn. data and production figures are given for the Goose Creek Orange and Hull crudes, Texas.

D. F. BROWN

Method of separating permanent gas greatly affects crude evaporation. J. H. WIGGINS. *Nat. Petroleum News* 14, No. 49, 29-32 (1922).—Generally speaking, small pressure traps, operating at considerable pressure, the time the oil and gas remains in the trap being only a few seconds, are more effective in holding down evapn. than larger tanks used as separators operating at atm. pressure.

D. F. BROWN

Evaporation of straight run gasoline in bare and insulated storage tanks. J. H. WIGGINS. *Nat. Petroleum News* 15, No. 1, 30 (1923); cf. C. A. 17, 333.—Distn. tests on straight run gasoline show an initial b. p. of 95° F. and when 0.5% had been

taken off the b. p. had been raised to 115° F. These temps. are so much above av. atm. temps. that insulation does not effect as great saving as in the case of compression gasoline. Actual tests show a slight advantage for the insulated tank but the total loss in both cases was small because of the small surface exposed, the small vol. of air above the gasoline (40 cu. ft.), and the facts that most of the very volatile fractions had already evaporated from the crude oil in the lease and pipeline tanks, the tanks were sheltered from the wind, and the tanks were tight with a restricted vent. D. F. BROWN

The mining of oil shales. W. C. RUSSELL. *Railroad Red Book* 39, 1051-5 (1922).—R. describes the Colorado shale deposits and discusses methods to be employed in mining the same. D. F. BROWN

Oil shale unsaturates. C. W. BOTKIN AND R. W. BOYD. *Petroleum Age* 10, No. 12, 26-7 (1922); cf. *C. A.* 17, 465.—Data presented on I absorption by the Hilbl-Waller method and H₂SO₄ absorption by shale oil show little relation between the two. Decompn. occurring during distn. under atm. pressure lowers the H₂SO₄ absorption of the crude oil considerably but affects the I no. but little. The substances undergoing a max. decompn. (shale, gilsonite, and shale oil residue) are markedly increased in I no. of the material, in the I no. of its acid-sol. content, and in the % of oil unabsorbed by H₂SO₄. The wt. of I absorbed by 1 g. of unsaturates is lowest for the heavier undecompd. materials (0.35, 0.48, and 0.57, resp., for gilsonite, ash-free shale material, and shale oil residue) and highest for the lighter products which have undergone more decompn. (0.81 to 1.39 for the crude shale oils and 0.89 to 1.88 for the once run oils). The decompn. apparently produces additional saturates, increases the I no. of the acid-sol. oil, and causes losses of N which are roughly proportional. It is thought that the saturates are the result of the breaking down of acid-sol. satd. materials. D. F. B.

Properties of typical crude oils from the producing fields of southern Texas. N. A. C. SMITH, A. D. BAUER AND N. F. LEJEUNE. *Bur. Mines, Repts. Investigation* No. 2416, 2 pp. (1922).—Of 38 samples taken 6 had gravities lighter than 30° A. P. I. (Baumé based on modulus 141.5), 5 had gravities between 25° and 30°, 10 between 20° and 25°, and 7 below 20°. S content varied between 0.2% and 2.2%. Striking peculiarity of crudes is almost complete lack of gasolene fractions. Pour tests were uniformly low, although viscosities were fairly high. Crudes are "naphthenic" in character, but not necessarily high in asphaltic content. C. T. WHITE

Sulfuric acid recovery in oil refineries. L. B. SKINNER. *Chem. Met. Eng.* 27, 734-6 (1922).—To obtain 20 to 25 tons of 66° Bé. acid from a 35° Bé. acid requires a series of 8 Pb pans with a combined area of 1,200 sq. ft., two cast-iron stills of about 50 sq. ft. area, and a condenser tower about 5 ft. square, and 18 ft. high. Scum must not be allowed to collect on the surface of the acid. A stream of inert gas passed over the surface of the liquid hastens vaporization. A preferred concentrator consists of four towers, one for evapg. weak acid, one for concg. to 66° Bé. acid, and two to condense the fume from the second tower. The hot gases of combustion come into direct contact with the acid. Draft is induced by an exhaustor. The concg. towers are packed with evenly spaced bricks. Construction details are given. The uniform distribution of the acid over the packing is important. A suitable distributor is described. The absorbing towers are loosely packed, and weak acid is circulated. Three h.p. is required to run the exhausting fan. E. H. LESLIE

Fire, steam and vacuum stills; specifications, efficiencies. H. S. BELL. *Nat. Petroleum News* 15, No. 1, 41-3 (1923).—The evapn. surface for the usual type of horizontal still may be taken as $\frac{2}{3}$ of the diam. multiplied by the length when the still is operated on the batch principle. Records show that 2.5 gal. of distillate per hr. per sq. ft. of heating surface may be depended upon. The area of the vapor line must be sufficient to permit free and unrestricted passage of the oil vapors and steam, if used, to the con-

densers at a rate sufficiently high to accommodate the full still capacity. Ordinarily the horizontal stills should have a diam. $\frac{1}{3}$ their length. A table of diams. and capacities is given. The chief difficulty with the tube still is from C deposits but this can be overcome by maintaining the velocity of the oil through the tubes at not less than 3.8 ft. per sec. At this velocity the throughput per day of a tube still is, for 2 in. 1200 bbls., for 4 in. 2700 bbls. and for 6 in. 10,500 bbls. Vacuum stills may follow the same general plate arrangement as the fire stills but are smaller and more strongly braced to avoid collapse. Tabular data of results from actual practice are given covering yield, fuel consumption, etc., for the different types of still. Methods of firing are discussed.

D. F. BROWN

The utilization of heavy fuel oils in internal-combustion engines. H. MOORE. *Oil Eng. and Finance* 2, 711-13(1922); cf. *Ibid* 689.—Bituminous substances in fuel oils coke instead of vaporizing; hard bitumens cause much more trouble of this sort than soft bitumens. Waxes offer no difficulties as to burning, but they tend to prevent sand, water, etc., from settling out of the fuel. Sulfur in these oils shows no corrosive effects. The effects of other impurities such as sand, water, iron rust, etc., are discussed.

D. F. BROWN

An experimental survey of gasoline and kerosene carburation. C. S. KERRIS AND G. A. YOUNG. *J. Soc. Automotive Eng.* 12, 63-75(1923).—Gasoline mixed with air preheated to 150° shows about equal thermal efficiency with kerosene at 250° but greater power. The max. thermal efficiency for both is shown at the theoretically perfect mixt. corresponding with about 0.067 lbs. of fuel per lb. of dry air. Kerosene shows higher cooling losses and lower exhaust gas loss temps. at half load than gasoline. 150° is the proper minimum temp. for the air inlet with either fuel.

D. F. BROWN

Distillation products of West African Woods. ANON. *Bull. Imp. Inst.* 20, 162-5 (1922).—Distn. tests carried out on *Silk-cotton wood* (*Eriodendron anfractuosum*) (1), "*Kaku*" or red iron wood (*Lophira procera*) (2), "*Odum*" (*Chlorophora excelsa*) (3), and *Umbrella wood* (*Musanga Smithii*) (4) gave the following results; previously obtained results for oak (5) (typical hard wood) and pine (6) (typical soft wood) are given for comparison:

	(1)	(2)	(3)	(4)	(5)	(6)
Wt. of material distd. (lb.)	2.5	6.5	4	1.5	3.5	3
Time required for distn. (hrs.)	3.5	4	5	1.67	3.5	3.25
Yield of	%	%	%	%	%	%
Charcoal	28.4	30.3	32.0	27.7	25.0	29.2
Crude pyroligneous acid containing	43.7	40.6	38.5	43.7	53.9	40.1
Acetic acid	2.0	2.4	2.4	3.7	4.4	2.2
Dissolved tar	4.6	3.8	2.9	3.7	5.8	5.1
Wood naphtha, MeOH, Me ₂ CO	1.5	1.2	1.3	1.4	1.3	0.9
Tar, separated	8.2	7.2	8.0	8.0	6.4	12.9
Containing AcOH	0.3	0.3	0.3	0.4	0.4	0.3
Total yield of tar	12.8	11.0	10.9	11.7	12.2	18.0
Total yield of AcOH	2.3	2.7	2.7	4.1	4.8	2.5

A. P.-C.

Factors affecting the use of air in oil-burning with comparison of cost. W. C. BUELL, JR. *Proc. Eng. Soc. Western Penn.* 38, 201-21(1922).—Industrial oil-burning equipment can be classified into 3 groups on the basis of the pressure at the source of air upon which they operate. The pressure ranges and designations are as follows: 4-12 oz., or "volume" air (high-speed fans, etc.); 12 oz.-2 lbs., or "positive" air (displacement or turbine-type machines); and 50-100 lbs. gage, "high-pressure" air (stand-

ard reciprocating compressors, etc.). All of the factors involved in the three systems are discussed. The first class of equipment is condemned, since mechanical atomization of the fuel is required, and this necessitates the use of non-viscous, clean distillates. The functions of air velocities, velocities found in combustion, and methods of reducing velocities are considered. The quantities of air needed for combustion, and the inductive properties of the primary air are considered. The performance of blowers is discussed in detail. The "cost" of air per gal. of fuel with compressor at 15 lbs./sq. in. is less than that of a 1 or 2 lb. turbine machine, but in spite of this fact, the latter will probably be the more economical machine in the majority of cases. Operation of 1 and 2 lb. turbine machines costs 0.002 and 0.0025 cents per gal. of fuel oil, resp. A 15-lb. machine adds a cost of 0.0015 cent per gal. to the fuel cost, and an 80-lb. machine 0.006 cent. Since a premium of a cent per gal. may be required for a fuel oil suitable for a "volume" air burner, it is seen that the use of "positive" air may effect considerable economy.

W. F. FARAGHER

Removal of resin from wood prior to the manufacture of cellulose (WENZL) 23. The origin of petroleum (HÖFER) 8. Apparatus for distilling shale, coal, wood or other carbonaceous materials. (U. S. pat. 1,437,292) 21. Extracting coal and separating hydrocarbons (U. S. pat. 1,436,289) 21.

BLUM, ANTHONY. *Petroleum: Where and How to Find It*. Chicago: Modern Mining Books Publishing Co. \$2.00. Reviewed in *Can. Chem. Met.* 6, 207(1922).

CROSS, ROY. *Handbook of Petroleum, Asphalt and Natural Gas*. Kansas City, Mo.: Kansas City Testing Laboratory. 625 pp. \$7.50. Reviewed in *Chem. Met. Eng.* 27, 1183(1922).

JAUCH, L. *Le pétrole et son industrie*. Paris: Augustin Challamel. Reviewed in *Giorn. chim. ind. applicata* 4, 120(1922).

Cracking petroleum oils. R. CROSS. U. S. 1,437,220, Nov. 28. Oil is cyclicly circulated through a heating pipe in a furnace to raise its temp. to that of cracking. Liquid oil at this temp. is then diverted into a larger insulated reaction chamber where it is maintained under pressure of the evolved gases sufficient to prevent vaporization of the bulk of the oil during completion of the cracking.

Oxidizing liquid hydrocarbons. G. TEICHNER. U. S. 1,436,214, Nov. 21. Galician spindle oil or a similar liquid hydrocarbon material is treated with fuming H_2SO_4 to remove substances which on blowing with air tend to form resinous or asphaltic compds. and the purified material is then blown with air at 125° in the presence of Zn stearate which serves as a catalyst for the production of saponifiable material.

Oxidizing liquid hydrocarbons. E. ZERNER. U. S. 1,436,136, Nov. 21. Raw gas oil or similar liquid hydrocarbons are freed from unsatd. compds. by treatment with liquid SO_2 ; the SO_2 remaining in the undissolved residue is evapd. and the purified product is treated with a current of air and with $Ca(OH)_2$ in order to effect oxidation and obtain fatty acids. Cf. *C. A.* 16, 2027.

Apparatus for purifying gasoline by filtration and sedimentation. F. V. ROSS. U. S. 1,437,153, Nov. 28.

Still for treating hydrocarbon oils. J. C. POOL. U. S. 1,436,526, Nov. 21. An inclined fire-tube still is connected with a settling chamber which is out of contact with gases from the heating furnace and serves to collect sludge and tar.

Asphaltic product from petroleum. L. KIRSCHBRAUN. U. S. 1,436,450, Nov. 21. Distillates which condense as heavy oils and a residue which is of asphaltic character

are obtained by distn. of petroleum residuum oil in a series of stills connected to primary and secondary condensers. The temp. of the secondary condensers is maintained below the b. p. of H_2O by passing H_2O through them and the temp. of the primary condensers is maintained at a temp. above the b. p. of H_2O by circulation of the cooling liquid from the secondary to the primary condensers.

23—CELLULOSE AND PAPER

CLARENCE J. WEST

Report of the Viscosity Committee of the Cellulose Division. G. J. ESSELEN, JR. *et al.* *J. Ind. Eng. Chem.* **14**, 1164-5(1922).—A proposed falling-ball method for use with cellulose esters. EUGENE C. BINGHAM

The constitution of cellulose. V. H. LEGG. *Fuel* **124**, 196-205(1922).—A review. C. C. DAYIS

Viscosity of cellulose. II. The lowering of the viscosity of cellulose by various reagents. R. A. JOYNER. *J. Chem. Soc.* **121**, 2395-409(1922); cf. *C. A.* **16**, 3543.—The effect of varying concn. of NaOH on sliver cotton when heated for 9 hrs. at various temps. was detd. The more dil. solns. of NaOH have a relatively greater effect than the more concd. ones; it is probable that the effect is due to the HO ions. These results are important in the kierung of cotton. The concns. of the NaOH used are generally not more than 4% and therefore the drop in viscosity can be found for any temp. between 100 and 40° for a kierung period of 9 hrs. From the extrapolated values it is seen that the max. value of the viscosity of cellulose is about 57,000 sec. or 28,000 C.G.S. units at 20° for a 2% soln. in cuprammonium hydroxide contg. 13 g. Cu and 200 g. NH_3 per l. It is believed that there are 2 kinds of cellulose, high-viscosity cellulose or "A", which has the high value, and a low-viscosity cellulose, "B", which has a viscosity of 1 sec. for a 5% soln. The action of N NaOH on cellulose at various temps. seems to follow the unimol. law. Sorption of NaOH takes place and is increased by the addition of neutral salts. Neutral salts alone had little effect on raw sliver at 120° but in conjunction with NaOH, KCl had an especially strong effect. The sorption of NaCl or KCl by cellulose from 22% soln. was small (about 1 g. per 100 g. cellulose). The effect of dil. HCl was studied. The temp. effect is large and the constant is probably proportional to the acid concn. Viscosity values show that the addition of a small amt. of air to the cellulose soln. brings about a great change, while further additions produce little effect. It is calcd. that 16 g. O will react with about 2100 g. cellulose, converting all of "A" into "B". Boiling cellulose with 4% NaOH for 0.75 hr. at atm. pressure during which time H_2O_2 was added, reduced the viscosity from 2160 to 1.7; the product had no Cu reduction no., and was, therefore, little degraded. The addition of 1.5 cc. N NaOCl per g. of cellulose in NaOH reduced the viscosity of a 4% soln. to 4 sec.; in Na_2CO_3 soln., 0.8 cc. N soln. reduced the viscosity to 2.5 sec. Since 16 g. O reacted with about 2500 g. cellulose in these expts., this means that the min. mol. wt. of cellulose must be at least 2500, should 1 atom of O react with 1 mol. cellulose. C. J. WEST

Removal of resin from wood prior to the manufacture of cellulose. H. WENZL. *Zellstoff u. Papier* **2**, 228-32(1922).—Methods depending on the use of petroleum hydrocarbons in which 90% of the total resin is extd. have been worked out, some of them depending on the use of high pressures and moderate temp. Chlorinated hydrocarbons are hardly suitable but tetralin appears particularly promising. The process of Benson and Bennett by the use of 70% EtOH (*C. A.* **16**, 1663) is of interest as a subsidiary of the sulfite spirit scheme, since much of the requisite plant is common to both. When the size of the wood particles is reduced to 25×45 mm., the extn. of 71% of the resin content has been effected. Methods depending on the use of emulsified org.

solvents have not been very successful in spite of the low cost, owing to the defective penetrating power of such emulsions. In one process molten rosin or pitch has been employed at 200° for the treatment of very resinous wood waste but the residual wood is rendered useless for cellulose manuf. A process of extn. with dil. NH_4OH at 70° has given high yields of resin but it is necessary to ext. the resin from the NH_4OH by means of gasoline and the double process is not economical. Many processes are based on the use of NaOH and Na_2CO_3 for the extn. of resin as a preliminary stage in the digestion of wood for the manuf. of kraft cellulose. By these methods, however, the chem. properties of the resin are profoundly modified. Sometimes very high pressures and moderate temp. are recommended on this account; the use of reducing agents such as hyposulfite and of an indifferent atm., such as H_2 gas, have also been proposed.

C. J. WEST

Determination of alkali-resistant cellulose. P. WAENTIG. *Zellstoff u. Papier* 2, 225-8(1922).—In the standard method for the detn. of α -cellulose in wood-pulp, the principal source of error is the repptn. of colloidal cellulose when the paste is diluted with H_2O before filtration. W. proceeds as follows: 3.5 g. of pulp is dried at 105°, weighed and steeped in a porcelain mortar with 50 cc. 17.5% NaOH for 45 min. at room temp., the mass being worked up with a pestle to a uniform paste. 50 cc. H_2O is then stirred in and the paste transferred to a Buchner funnel, 8-10 cm. in diameter, covered with a fine cotton cloth filter. It is washed on the filter with 200 cc. of 8% NaOH and sucked as dry as possible. The cake of cellulose is treated with 50 cc. 5% AcOH , again sucked dry, transferred back to the mortar, broken up and stirred again with a further 50 cc. of 5% AcOH . The cellulose is then collected on the filter, washed until neutral to litmus, and dried on a watch glass and then at 105° in a stoppered weighing bottle until const. wt. is reached. The results are expressed in terms of dry substance. This method generally yields values 2-3% lower than the older method, presumably because of the longer contact with the NaOH and the more thorough washing out of the colloidal cellulose with the 8% NaOH , but it is contended that the results are more uniform and are obtained under conditions corresponding more closely with those of practical mercerization in the viscose industry.

C. J. WEST

The chemical composition of Swedish pulps and methods of analysis of pulps. RUDOLPH SIEBER. *Zellstoff u. Papier* 2, 253-8(1922).—Analytical results are given for 14 different Swedish pulps, including ash, resins and fat, furfural, pentosans, lignin, cellulose according to Schwalbe and Johnson, baryta-resistant cellulose, corrected Cu no., Me no., loss upon treatment with $\text{C}_6\text{H}_5(\text{OH})_2\text{AcOH}$ and the baryta-resistant content of S. and J.'s cellulose. S. also compares the phloroglucinol and the barbituric acid methods for detg. furfural. The values obtained by the latter method are considerably lower; this may be due in part to the formation of decompn. products during the distn. with HCl which are pptd. by phloroglucinol but not by barbituric acid. The detn. of lignin may be greatly shortened by the use of warm (30-35°) 72% H_2SO_4 .

C. J. WEST

The use of rotten and stained wood in the manufacture of sulfate pulp. E. SUTER-MEISTER. *Pulp & Paper Mag. Canada* 20, 513-4(1922).—Rotten wood undergoes unusually large losses during the prepn. of chips and suffers in the amt. and quality of fiber it produces. The pulp from the sound wood was of a good light color while that from rotten wood was much darker and full of brown shives. The yield per cord was 787 lbs. for rotten wood and 956 lbs. for sound wood. The unbleached fiber from rotten wood was weaker and practically unbleachable. River-driven wood, stained a grayish brown color from the bark, was cooked for 10 hrs. at a max. pressure of 75 lbs. The yield did not suffer in comparison with that of unstained wood, but the fiber was darker in color and was full of dark-colored shives. For bleaching pulp from stained wood 15.7% bleach was required, from sound wood 8.6%.

H. H. HARRISON

Colloid-chemical investigations of sulfite liquors. I. Mode of occurrence of sulfurous acid in sulfite waste liquors. M. SAMMC AND M. REBER. *Kolloidchem. Beihefte* 16, 215-33(1922).—The mode of occurrence of H_2SO_3 in the sulfite waste of liquor is detd. by the reactions of the carbohydrate sulfonic acids and the lignosulfonic acids. The amt. of "free" H_2SO_3 is increased by the addn. of alkali and is decreased by the addn. of acids and bisulfites. $AcONa$ also increases the amt. of free H_2SO_3 , the amt. in a N soln. increasing to 0.81%. With increasing diln. the relative amt. of "free" H_2SO_3 is increased, being relatively greater in acid than in a neutral soln. Excess alkali or $AcONa$ will also liberate H_2SO_3 from the sulfonic acids. The condition of equil. is more quickly reached in a neutral than in an acid soln. The influence of external factors upon the equil. is variable and often the reverse of the expected. C. J. W.

Analytical methods for sulfite liquors. RUDOLF SIEBER. *Zellstoff u. Papier* 2, 199-201(1922).—Good results are obtained for free acidity by Höhn's method, using methyl red instead of phenolphthalein as indicator. The combined H_2SO_3 cannot be calcd. accurately from a detn. of the total Ca , because the suggested correction for SO_4 of 0.16% is not a reliable const. The detn. of the SO_4 cannot be omitted when carrying out Sander's method and it is necessary to work in an atm. of CO_2 . This can be generated in the reaction flask from Na_2CO_3 , the corked flask being provided with a small dropping funnel and a delivery tube dipping into a beaker of water. HCl is 1st introduced through the dropping funnel into the Na_2CO_3 and when all the air has been expelled the sulfite liquor is introduced through the funnel. Oxidation of the H_2SO_3 might be inhibited by a negative catalyst, such as $SnCl_2$ and the necessity of a CO_2 atm. might thus be avoided. S. has devised a method for the rapid filtration of $BaSO_4$ by means of a filter pump. For this purpose the filter plate is covered with a thick paper filter and a measured amt. of a suspension of kieselguhr of exactly known concn. is first distributed over the filter with very gentle suction. This forms a bed which retains the $BaSO_4$ completely even when freshly pptd. and filters very rapidly. A correction is made for the wt. of the dry ignited kieselguhr. In the spent liquor the completely free H_2SO_3 is detd. by distn. without acidification; this is better than the direct titration with I . Total S in spent liquor is detd. by a Na_2O_2 method: 5 cc. of the liquor is treated with concd. $NaOH$ in a Ni crucible and the alk. liquid evapd. to dryness. A mixt. of 3 g. each of Na_2CO_3 and Na_2O_2 is mixed with the powdered residue and carefully heated over a small flame. Afterwards a further 0.5 g. of Na_2O_2 is added and the mass brought to fusion. SO_4 is then detd. in the melt after treatment with Br .

C. J. WEST

Analytical data for the paper industry. N. FOLKE BECKER. *Paper* 30, No. 7, 38-44(1922).—See *C. A.* 16, 3392.

H. H. HARRISON

Microscopic analysis of fibers in paper. H. N. LEE. *Paper Ind.* 4, 928f; *Paper Trade J.* 75, No. 22, 47-9(1922).—A brief description of the various methods of fiber analysis.

H. H. HARRISON

Use of rubber in paper manufacture. FRED. KAYE. *Paper* 30, No. 7, 29-32; *Paper Maker* 64, 447-52(1922); cf. *C. A.* 16, 1150.

H. H. HARRISON

Chlorine in paper making. ISMAR GINSBERG. *Chemical Age* (N. Y.) 30, 487-8; *Paper* 31, No. 8, 10-11(1922).—This is a review of the Pomilio pulping process.

C. J. WEST

Paper dyeing. EMIL HEUSER. *Paper Maker* 64, 433(1922); cf. *C. A.* 16, 2601.—Of the commoner filling substances, such as kaolin, talc, asbestos and blanc fixe, the acid silicates absorb most readily basic and substantive dyes, while acid dyes are absorbed by them in much smaller amts. The best absorbent is asbestos, the most refractory $BaSO_4$. Acid dyes used in connection with silicates and blanc fixe can be washed out; acid silicates treated with basic and substantive dyes are quite fast. Ex-

cellent results were obtained by producing the filler in the beater from water glass and $\text{Al}_2(\text{SO}_4)_3$, CaCl_2 , MgSO_4 , etc.

H. H. HARRISON

A new process for determining the degree of fineness of beaten stuff. E. W. L. STARK. *Paper Trade J.* 75, No. 21, 53-5(1922).—See C. A. 16, 3756.

H. H. HARRISON

Moisture influence on tests of container board. S. D. WELLS. *Paper* 31, No. 7, 7-9; *Paper Trade J.* 75, No. 23, 47-49; *Paper Ind.* 4, 1245-7(1922).—The change in pop test is directly proportional to the moisture content in container board. With paper the folding test increases with the moisture content as does the toughness when measured by the tearing test.

H. H. HARRISON

Sulfite alcohol (DELABY) 16. Cellulose chemistry (HIBBERT, HILL) 10. Nitro-cellulose solution (U. S. pat. 1,437,170) 26.

CROSS, CHAS. F. and DORRIS, CHAS. Researches on cellulose, IV. (1910-1921.) London: Longmans, Green & Co. 252 pp. 15s. Reviewed in *Chem. News* 125, 127 (1922); *Mech. Eng.* 45, 148; *Nature* 111, 12(1923).

Nitrating cellulose. R. P. CALVERT. U. S. 1,437,041, Nov. 28. A thin sheet of paper is subjected to high compression, shredded and then nitrated. The preliminary compression lessens the amt. of nitrating acids required.

Testing paper or other fibrous material. G. L. SCHNABLE and F. F. ABBOTT. U. S. 1,436,323, Nov. 21. Paper or similar material is subjected to friction by drawing it over stationary plates and simultaneously subjected to a repeated folding until sepn. of the material occurs.

24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

Safety explosives. HOORWAERTS. *Rev. univ. mines* July 1922; *Technique moderne* 14, 477-8(1922).—The difference between the time of retardation of inflammation and the length of time required to cool the gases below the ignition temp. of the CH_4 is a measure of the true safety of a blasting explosive. The av. max. charge of 13% safety explosives has been increased in 20 yrs. from about 69 g. to 900 g. The most successful method of increasing this max. is that of Lemaire; it consists in surrounding the cartridge with a coating of 50% CaF_2 and 50% plaster, which is volatilized by the explosion and extinguishes the greater part of the flames before they have a chance of coming in contact with the atm. The force of the explosive is decreased by but a few %.

A. P.-C.

Determination of mixed acid (PATTERSON) 7. Testing mine dusts (WHITTAKER) 21.

Explosive priming mixture. J. E. BURNS. U. S. 1,437,224, Nov. 28. A priming mixt. for small arms ammunition is formed of KClO_3 30, $\text{Pb}(\text{NO}_3)_2$ 12, $\text{Pb}(\text{SCN})_2$ 33 and powd. glass 25 parts.

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

Absorption colors of the second order. JEAN PICCARD. *Rec. trav. chim.* **41**, 581-4(1922).—The simplest dyes are yellow. When changes in constitution are made such as substituting NH_2 with MeNH the color passes from yellow to orange, then to red, violet, blue and finally green (Nietzki's rule). P. (C. A. **5**, 3444) passed beyond the green by prep. merquinone diimonium salts by oxidizing $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$. Willstätter and P. (C. A. **3**, 70) obtained $\text{MeNHC}_6\text{H}_4\text{NH}_2$ (orange); the di-Me deriv. (red); the tri-Me deriv. (violet); the tetra-Me deriv. (blue-violet); the di-Ph derivs. (blue) and the tetra-Ph deriv. (green). A similar series from benzidine is known in which the tetra-Me deriv. is green, the di-Ph deriv. is yellowish green and the tetra-Ph deriv. (A) is yellow (C. A. **7**, 2939). These recurrences of a 2nd series of colors with increasing complexity are called "color of the second order," which is defined as the color of a substance belonging to a group of dyes of which the parent compds. have already passed through the entire series of colors from yellow to green. A hypothetical interpretation of this phenomenon is offered. P. undertook to extend the series by oxidizing heavier mols. than that of A. Diphenylbisphenylbenzidine oxidized in glacial AcOH gave a red merquinoid dye. From this it appears that Nietzki's rule also applies to color of the 2nd order. Of course the colors of the 2nd order are not always developed. When the constitution of the dye is too complicated to produce a simple spectrum the browns and blacks are formed, such as aniline black. E. J. W.

Catalytic reduction of indigo. ANDRÉ BROCHET. *Rev. gen. mat. color.* **27**, 131-6 (1922).—Ni precip. according to Sabatier and Senderens was used as the catalyzer. Forty g. of indigo and 20 g. of the active Ni were suspended in 170 cc. of H_2O to which 25 cc. NaOH (36° BÉ.) was added and the mixt. placed in a 500 cc. Woulf bottle supplied with necks for the admission of H_2 , a thermometer and an exit tube. The app. was placed on a shaker and the temp. was controlled by an electric heater. H_2 under regulated pressure, was admitted in measured amts. with the temp. between 45° and 60°. Air was at first swept out by H_2 , the air exit then closed and the app. made tight. The reduction of the indigo was complete in 30 to 40 min. according to the activity of the Ni employed. The amt. of H_2 required was substantially that required by theory. During the first 10 min. the absorption of H_2 averaged about 140 cc. per min., when nearly one-half of the H_2 required was absorbed. Different samples of indigo varied in their rate of reduction during the first 30 to 35 min. but after 40 min. were practically const. The Ni appears to retain its activity for several months, the older samples being less active during the first 5 min. of operation but more active after 15 min. Applications of the method to the reduction of other substances are discussed. L. W. RIGGS

Testing dyes and their fastness to light under the quartz-mercury arc lamp. S. W. ROBINSON. *Am. Dyestuff Rept.* **11**, 384-6(1922).—The water-jacketed quartz lamp and the quartz light radiometer are described, illustrated and their uses for testing fastness of dyes are discussed. Summary of the progress made to date by various investigators in an effort to standardize methods for determining the fastness of dyes to light. W. H. CADY, *et al.* *Ibid* 382-3.—The problem may be divided into standardizing the source of light and measuring and recording the amt. of fading. The sun as a source of light is unsatisfactory because the intensity of the light and radiant energy received is constantly changing. Other conditions such as presence of moisture, fumes, etc., change during an exposure. Sun fading is too slow, especially in winter. The artificial sources of light and the standards of fading so far in use are described. Much further investigation is needed to place the detn. of fastness on a satisfactory basis.

L. W. RIGGS

Lime in the dyehouse. E. R. DARLING. *Am. Dyestuff Rept.* 11, 323-5(1922); cf. C. A. 16, 2783.—Lime in the textile industry is used on a large scale for the lime boil, softening water, recausticizing waste caustic liquors, and on a smaller scale for liming kiers, dyeing, prepn. of chemie and the scouring of wool. Directions for performing the lime boil, liming of kiers and wool scouring are given. Lime for use in the textile industry should be low in Mg, Si and Fe, though Fe in small amts. does not color the goods as is generally assumed. CaO should be at least 94%, Mg(MgO?) less than 2.5%, SiO₂ not more than 3% and not over 2% of Al₂O₃ + Fe₂O₃. Limes used in dyeing should contain less than 1% of Fe₂O₃. Lime is cheap, safe to handle, reduces the number of uneven boils, removes wax and protein matter, reduces time required when the pressure kier is used and is milder in action than the other alkalis.

L. W. R.

Practical dyeing of cotton piece goods. M. W. ALLING AND C. L. BRAINERD. *Am. Dyestuff Rept.* 11, 369-72(1922).—Since time is the important element in machine production, all details possible should be worked out before the actual dyeing operation on a given piece begins. A carefully planned time schedule should be made and closely followed. Various machines, dyes and continuous processes for large scale operations are described.

L. W. RIGGS

Dyeing cotton piece goods on the padder. W. F. DEADY. *Am. Dyestuff Rept.* 11, 333-4(1922).—The padding machine and its method of operation are described. The padder offers the quickest and simplest means of producing plane colors on cotton piece goods with direct dyes, and is the most extensively used machine in a finishing plant for the dyeing of light and medium shades.

L. W. RIGGS

Dyeing mixtures containing artificial silk. GEORGE EMMONS. *Am. Dyestuff Rept.* 11, 268-74(1922).—Emphasis is laid on the properties of acetyl silk and the methods of dyeing it by the Clavel system. **Dyeing wool-silk materials the same shade.** *Ibid* 399-401.—A list of 34 acid dyes suited to the simultaneous dyeing of wool and silk is given with general directions for their use. Temp. control is an important factor in this class of dyeing. In general dyeing should begin in the cold, and the temp. should be kept under 95°. Basic dyes for wool-silk mixts. are briefly described. **Bleaching and dyeing Tussah silk.** *Ibid* 463-7.—The characteristics of Tussah silk are stated and its differences from mulberry silk are indicated. For bleaching the fiber the H₂O₂, Na₂O₂ or perboric acid bath is used. This variety of silk has a greater affinity for dyestuffs than mulberry silk. The rapidity with which it absorbs dyes is the cause of difficulty in dyeing this silk evenly. Recipes and details for dyeing are given.

L. W. RIGGS

Multicolor effects in simple piece dyeing. REX CROSS. *Am. Dyestuff Rept.* 11, 377-8, 389-90, 431-3(1922).—Cloth made from different fibers such as cotton, wool and silk can be dyed in one bath with a different color for each fiber. Multicolored effects in pieces from one kind of fiber can be produced by dyeing the fiber or yarn before weaving or by printing. Directions for producing heather mixts. and other effects are given. Areas of cloth treated with acids or alkalis will dye differently from the adjacent untreated areas.

L. W. RIGGS

Dyeing sweat pad goods. J. WILKINSON. *Am. Dyestuff Rept.* 11, 357-61(1922).—But 2 colors, brown and yellow, are used for dyeing sweat pads for horses. The shade of color must be uniform in every bale because the goods are mixed and cut up and variations of shade spoil merchantability. For the same reasons different lots must have the same shade. Substantive colors are preferred and the goods are dyed directly from the bale on a padding machine. For brown, to 50 gal. of boiling water is added Diphenyl Brown 2 lbs., Chicago Brown 1, soap 5, Glauber salt 10, apparatus 2 pails. Boil and while boiling run 1500 yards of goods through twice. Before the beginning of the second run the dye box must be filled with water to its original height. For

the second and before each subsequent batch of goods add to the old dye liquor Diphenyl Brown 30 oz., Chicago Brown 12 oz., soap 2 oz., Glauber salt 10 oz., apparatine 2 pails. For the yellow color use Diphenyl Yellow 2 lbs., soap 5, Glauber salt 10, apparatine 2 pails. For the second and subsequent batches of 1500 yards, add to the old liquor Diphenyl Yellow 1.5 lbs., soap 3, Glauber salt 10, apparatine 2 pails. The various materials mentioned in these recipes are separately dissolved in a stock soln. so that a 12 quart bucketful (or multiple thereof) will contain the wt. required. Adding dry dyes to the dye box is wasteful. After dyeing the goods are dried under tension on a cylinder drying machine. The combination of drying and finishing machines as described will handle 30000 yards daily. L. W. RIGGS

Preparation of woollens for piece dyeing. C. A. EVERETT. *Am. Dyestuff Rept.* 11, 300-1(1922).—Directions are given for prepg. soaps for fulling, the process of fulling, manipulation of the fulling machine, handling the goods in the washer and carbonizing.

L. W. RIGGS

Hosiery dyeing. A. T. BRAINERD AND W. E. BRAINERD. *Am. Dyestuff Rept.* 11, 441-6(1922).—The problems of the hosiery dyer are discussed. Modern machinery for dyeing hose on a large scale is described. L. W. RIGGS

Bleaching and dyeing jute. ANON. *Am. Dyestuff Rept.* 11, 319-22(1922).—The properties of jute fibers and their prepn. for manuf., bleaching, dyeing and printing are described. L. W. RIGGS

Sodium peroxide a bleaching agent. W. B. NANSON. *Am. Dyestuff Rept.* 11, 419-23(1922).—In the prepn. of a bleaching soln. Na_2O_2 should be added slowly to cold water with const. stirring, the temp. being kept below 40° . The NaOH formed is then neutralized by a slight excess of H_2SO_4 and the bath brought back to faint alkalinity by NH_3 . Na_2O_2 is specially adapted to bleaching wool and cotton-wool mixts. A bath recommended for fine cotton goods, laces, etc., contains water 100 gal., H_2SO_4 (168° Tw.) 10.25 lbs., Na_2O_2 8, Na_2HPO_4 0.25. This bath is made slightly alk. with NH_3 , and heated to 50° when the goods are entered and worked. Applications of Na_2O_2 to bleaching other materials are described in detail. **Chromates of lead in dyeing and calico printing.** *Ibid* 467-71.—The properties of chrome yellow, chrome orange and chrome green are described with reference to their dyeing values. Directions are given for the prepn. and application of dark ambers, light straw, lemon yellow, chrome amber, dark chrome yellow and chrome yellow. L. W. RIGGS

Flax (retting by the Kayser process). ANON. *Bull. Imp. Inst.* 20, 363(1922).—Retting takes place at $25-28^\circ$. After the action has commenced, sufficient heat is evolved to maintain the temp. The organism rapidly attacks pectic matter, but has little action on the true fiber substance. Retting takes place with great regularity and occupies the same length of time (60-72 hrs.) whatever the depth of the tanks or the amt. of straw immersed, provided the layers do not exceed a total thickness of 10-11 ft. The time could probably be considerably reduced. The method is being used commercially with excellent results, with a 14-17% yield on the wt. of the straw. It is suitable for hemp, and probably for other fibrous materials. A. P.-C.

The retting of plants. L. BOUTARD. *Rev. textile* (Nov. 1921) p. 1570; *Industrie chimique* 9, 502(1922).—Esparto, which is reputed to be non-rettable, can be readily retted if it is in contact with chicoraceous or leguminous plants. The water of certain streams has retting properties because they pass through areas wooded with conifers and plains contg. chicoraceous and leguminous plants, the seeds of which are carried by the wind into the water. A. P.-C.

Chlorides in warp sizing. HOWARD FILE. *Am. Dyestuff Rept.* 11, 338, 356-7(1922).—Ca, Mg and Zn chlorides used in sizing preps. break down under the action of heat and moisture liberating HCl or Cl , which attacks the fiber. CaCl_2 is least harm-

ful in this respect. The damage appears when the goods are singed or bleached. If the goods are to be singed $MgCl_2$ and $ZnCl_2$ should be absent. L. W. RIGGS

Chemical reactions of the different kinds of artificial silks. ANON. *Avenir textile* (Feb. 1922); *Industrie chimique* 9, 503(1922).—A list is given (in the original article but not in the Fr. abstract) of the reactions of Chardonnet, cuprammonium, viscose, and cellulose acetate silks, with various reagents. A. P. C.

A clinical study of fur cutters and felt hat workers. W. WRIGHT. *J. Ind. Hyg.* 4, 296-304(1922).—Of a group of 103 hatter's, fur workers, makers and finishers in reasonably good health, 43% were considered to be in some degree poisoned by Hg.

H. B. LEWIS

Viscosity of cellulose (JOYNER) 23. Preparation of *d*-pinic acid (KNECHT, HIBBERT) 10. Dyes derived from "saccharin" (DUTT) 10. Red sulfide dyes. Mercaptan derivatives of azo dyes (WATSON, DUTT) 10.

AURET, CAMILLE. *Annuaire de la teinturerie française*. Paris: 16 rue Condorcet. Reviewed in *Rev. gen. mat. color* 27, 111(1922).

CARR, JOHN CANNELL. *Manufacture of Dyes*. New York: Textile Colorist, 53 Park Pl. \$4.50. Reviewed in *Textile Colorist* 44, 739.

MOHLAU, R. AND BUCHERER, H. T. *Farbenchemisches Praktikum*. 2nd Ed. Leipzig and Berlin: Vereinigung wissenschaftlicher Verleger. Reviewed in *Giorn. chim. ind. applicata* 4, 121(1922).

Principles and Practice of Fur Dressing and Fur Dyeing. New York: D. Van Nostrand Co. 190 pp. Reviewed in *Can. Chem. Met.* 6, 184(1922).

Apparatus for making filaments of artificial silk. W. P. DREAPEK. U. S. 1,437,340, Nov. 28. The app. is adapted for forming threads or filaments in a pptg. soln. U. S. 1,437,341 specifies winding artificial silk in untwisted condition, treating it with washing liquid and then stretching, dyeing, drying and cutting.

Apparatus for impregnating fiber with tar. F. B. STRATFORD. U. S. 1,436,735, Nov. 28. The app. is adapted for prepg. oakum.

26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

Sanitary conditions for workers in factories producing lead pigments and paints during 1920-21 in Germany. K. B. LEHMANN. *Zentr. Gewerbehyg.* No. 2 (1922); *Zentr. ges. Hyg. Grenzgebiete* 267(Jan. 25, 1922); *Bull. office intern. d'hyg. pub.* 14, 994(Aug. 1922).—Results of a personal inspection are given. Air of factories contained 0.2-0.4 mg. Pb per cu. m., corresponding to the intake of 0.4-16 mg. Pb per day. In feces the av. was 0.9 mg. Pb. These quantities are without apparent serious danger. There were indications of Pb poisoning in 9 out of 400 workers. Improved hygienic conditions in plants have reduced Pb poisoning in the last few years.

JACK J. HINMAN, JR.

Anticorrosive and antifouling composition. P. E. BOWLES. *J. Soc. Chem. Ind.* 41, 492-5R(1922).—The most satisfactory anticorrosive paints are solns. of certain pitches and asphalts in tar-oil solvents contg. Fe oxide pigments. Antifouling paints are usually resin solns. ground with Fe oxides and salts of Cu, Hg, or As. Electrolytic CuO is a less effective antifouler than pptd. CuO . Hg is best added in the form of org. salts which give consistently better results than $HgCl_2$ and permit a given quantity of Hg to be spread over a larger area. Arsenic except in complex compds. with Cu, such as in emerald green, appears to be practically useless. Illus. • F. A. WERTZ

Improving the quality of paints. W. T. PEARCE. *Paint, Oil and Chem. Rev.* 23, 10(1922).—An outline of the paint and varnish work carried on at the North Dakota State College. The value of the State paint-labelling law is reflected in the fact that the inert pigments in all samples taken by inspectors throughout the State averaged only 18%.

F. A. WERTZ

A rapid method for the determination of the amount of oil in oil paints. HANS WOLFF. *Farben-Ztg.* 28, 411-12(1922).—For factory control work, the quantity of oil in a paint can be detd. by weighing 3 to 5 g. of the paint, adding 15 cc. xylene, 10 cc. alc., 1 to 2 drops of HCl, and then exactly neutralizing. The sapon. no. is then detd. in the usual way, and the amt. of oil calcd. by using 185 as the av. sapon. value for oil. If the pigments present are decidedly basic, 3 successive portions of xylene-alc. mixt. are decanted from the pigment portion, and the sapon. no. is detd. on the ext. Accurate results are reported.

F. A. WERTZ

Testing small quantities of solvents especially those used in oil varnishes. HANS WOLFF AND CH. DORN. *Farben-Ztg.* 28, 330-31(1922).—When only a very small quantity of a solvent is available, the best method of identification is by its n_D , and dispersion detd. with an Abbe instrument. Tables give the various solvents and mixts. possible within certain ranges of refractometer readings. Turpentine and pine oils can be detected by the reaction of their peroxides with KI soln. Relative evapn. rate in comparison with pure xylene gives valuable information. Preliminary expts. on the detn. of b. ps. of solvents in capillary tubes give promise that this test is of value. Cf. following abstr.

F. A. WERTZ

The examination of small amounts of varnish solvents. HANS WOLFF. *Z. deut. Oel-Fett-Ind.* 42, 710-2(1922); cf. preceding abstr.—W. has worked out an approx. quant. procedure for analyzing solvents in varnish when only small amts. of the latter are available (5 cc. or less). The app. consists of a 5-10-cc. distg. flask with a small dephlegmator attached whose 30-40-cm. delivery tube serves as condenser, and in the outlet of the latter a bent wire is inserted to facilitate the flow of the distillate. Capillary pipets drawn out into a long capillary and divided into 1/100 cc. are used for measuring. Measuring flasks are made from capillary pipets whose end is blown out into a bulb. The separatory funnels are made from five 20-cc. pipets, cut off a little below the bulb and closed by a rubber tube carrying a glass head; the liquids are drawn off by removing this rubber tube at the bottom and closing the top of the pipet with the finger. The analytical procedure includes detns. of sp. gr., n and dispersion, extn. of the solvent by a 10% NaCl soln. and fractional distn. of the resulting 2 layers. The distillates are further examd. for identification, the detailed steps being described. A table shows d_{15}^4 , n_{20}^D , dispersion, b. p. and sapon. no. of 24 solvents. P. ESCHER

The temperature coefficient of the refractive index of American turpentine. GARTHA THOMPSON. *Analyst* 47, 469(1922).—Detns. are given for 4 samples of the best grades of Am. turpentine. A Pulfrich refractometer was used with a temp. range of 14-60°. The n_D value of the 1st sample was 1.47149 at 20.5°, 1.46272 at 39.2° and 1.45420 at 57.4°. The mean temp. coeff. was 0.000468. Analogous results were obtained for the other 3 samples, with mean temp. coeffs. of 0.000469-0.000470. There was little if any tendency for the temp. coeffs. to alter with the temp. C. C. DAVIS

China wood oil specifications. E. W. FISIG, et al. *Paint, Oil, and Chem. Rev.* 74, No. 24, 10-11, No. 25, 10-11, No. 26, 10-12(1922); 75, No. 1, 10-11, No. 2, 10-11(1923).—In attempts to draw up a standard specification for China wood oil, acceptable both to importers and consumers, criticism of the Am. Soc. Testing Materials specification (C. A. 14, 3804; 15, 3884) was invited from all interests. Replies, given in detail, indicate that the A.S.T.M. specifications, excepting the heat test, are fairly acceptable. The modified Browne heat test, if retained, should be supplemented by

the open-dish Worstall test (C. A. 7, 269), in which the character of the solid polymerized gel, and its color, can be observed. F. A. WERTZ

The analysis of oil varnishes. CH. COFFIGNIER. *Chimie et industrie* 8, 989 (1922).—Very brief outline of the more important detns. in the analysis of oil varnishes: solvent, oil, resins, ash, rosins; and of their reliability. A. P. C.

Formation of wax, resin and coloring matter in the Coccidae. The building up and breaking down of shellac. A. TSCHIRCH. *Chem. Umschau Fette Oele Wachse Harze* 29, 349-52(1922).—While plants are able to synthesize resins with C groups of the aromatic series, the animal body is only capable of forming compds. of the aliphatic series. Shellac consists principally of a resin, a wax, and some coloring matter. The resin is secreted from glands distributed over the whole surface of the insect, while the wax is secreted from localized glands. The red coloring matter has its origin probably in the activity of certain red bacteria in the body of the insect. The resin and the wax are actually built up by the animal and are not absorbed from the plant sap ready-made. The constituents of shellac may be sepd. from each other by first extg. the powd. substance with H_2O until the latter becomes colorless. The aq. red soln. is pptd. with Pb acetate, which ppts. the color from the sol. albuminous substances and sol. carbohydrates; it can be extd. from the Pb ppt. by alc. contg. some HCl, from the concd. HCl ext. the coloring matter crystallizes at 0° in clusters of leaflets as *laccic acid*, $C_{20}H_{14}O_{10}$, which cannot be sublimed. It contains a side chain which is being further investigated. The shellac is next extd. with alc., which quantitatively removes the resin together with a small amt. of some volatile aromatic compd. and a little golden yellow coloring matter. The alc. soln. is poured into H_2O acidified with HCl, the pptd. resin is washed, dried, powd. and extd. with ether, which removes the volatile aromatic compd. and the yellow coloring matter, crythrolaccin, which crystallizes out on concn., or still better from an alc. soln. of this cryst. residue; it can be sublimed. The residue from the ether extn. is aleuritic acid and may be redissolved in alc. and obtained as its Na salt, colorless plates. The shellac residue remaining after the alc. extn. is treated with xylene, which quant. removes the wax, sol. in very dil. NaOH and resembling laccinic acid; it probably is an absorption compd. of the latter. P. ESCHER

Synthetic resins: formo-naphthenic derivatives and their applications. ALBERT HUTIN. *Rev. prod. chim.* 25, 797-8(1922).—A comparison of the Badische, LaVingtrac, and Folchi processes, and of the properties and compn. of the products obtained by each. A. P. C.

Furfural resins. J. P. TRICKEY, C. S. MINER AND H. J. BROWNLER. *Ind. Eng. Chem.* 15, 65-6(1923).—A general survey and bibliography of the various furfural resins is given, with special reference to the phenol-furfural type. For the most infusible and insol. resins the proportions should be slightly in excess of 1 mol. furfural to 1 mol. phenol, and 0.6% HCl. With 1% Na_2CO_3 , H_2O as catalyst, 1.25 mols. furfural to 1 mol. phenol produced on a commercial scale, excellent infusible cold-molded products. This is contrary to results obtained by Beckman and Dehn (C. A. 14, 642). F. A. WERTZ

WALTER, GUSTAV ADOLPH. Die geschichtliche Entwicklung der rheinischen Mineralfarbenindustrie vom Beginn des 19 Jahrhunderts bis zum Ausbruch des Weltkrieges. Vol. VI. Essen: G. D. Baedeker.

WOLFF, H. Die Lösungsmittel der Fette, Oele, Wachse und Harze. Stuttgart: Wissenschaftliche Verlagsgesellschaft m.b.H. M 75. Reviewed in *Farben-Ztg.* 27, 2706(1922).

Paint. N. N. RANKOW. U. S. 1,436,356, Nov. 21. A paint adapted for use on

metal or tarred roofing is formed of linseed oil 3 pints, turpentine 1 qt., terebene 2 oz., black japan 2 oz., Venetian red 2 lbs. and Pb_3O_4 4 lbs.

Titanium pigment. V. M. GOLDSCHMIDT. U. S. 1,436,164, Nov. 21. A pigment comprising CaSO_4 and a solid soln. of Ti oxide in Ca titanate is prepd. by beating CaCO_3 with crude pptd. titanic acid obtained from a soln. from ilmenite and H_2SO_4 .

Paint containing rubber. S. R. TREVOR. U. S. 1,436,736, Nov. 28. Rubber is dissolved in linseed oil or a similar oil at a temp. of $140-170^\circ$, the rubber and oil mixt. is heated to $260-310^\circ$ and after cooling is mixed with a smaller amt. of H_2O to form a paint.

Fire-resisting composition. C. E. WELLES. U. S. 1,436,618, Nov. 21. A fire-resisting mixt. adapted for addn. to ordinary paints is formed of ZnO 1-2 lbs., air-slaked lime 1-2 lbs., linseed oil 1 qt., H_2O 1 pint, kerosene 1 pint, "sol. glass" ($30-35^\circ$ B \acute{e} .) 2-4 oz. and molasses 1-2 oz.

Printing process ink. G. W. BRENNER and C. C. HUTSON. U. S. 1,436,856. Nov. 28. An ink adapted for expansion by beating after drying is formed of yellow dextrin 10, NaHCO_3 1, a pigment 0.5 part and H_2O .

Nitrocellulose solution. C. W. CROCKETT. U. S. 1,437,170, Nov. 28. A compn. adapted for use as a lacquer or varnish is formed of nitrocellulose, mesityl oxide, EtOAc and C_6H_6 , with or without other solvents.

Varnishes. H. PLAUSON. U. S. 1,436,820, Nov. 28. A varnish base and dispersion medium, e. g., ebonite or soft rubber waste, xylene, limonene and NH_3 -olein soap are ground together under a peripheral disintegrator speed of about 2000 meters per min. or over, to form uniform suspensoid colloid solns.

27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

Review of progress in the chemistry of fats and oils. L. *Mat. grasses* 14, 6316-20 (1922). A. P.-C.

Report on fats and oil to the A.O.A.C. by its referee, G. S. Jamieson. H. S. BAILEY. *Cotton Oil Press* 6, No. 8, 30-1 (1922).—The A.O.A.C. referee on fats and oils for 1922 discusses the A.S.T.M., A.O.A.C. and A.C.S. action on standard procedures for the detn. of I no. He recommends that the Wijs soln. be made with Cl_2 not ICl_3 , as this latter reagent is unstable. A study of the I value obtained in the Hanus method after a $\frac{1}{2}$ and $\frac{3}{4}$ hour reaction periods, with linseed, soy bean, cottonseed, mustard seed and neat's foot oils indicates that nothing is to be gained by using the longer time. Some pure olive oils give a positive pink color which may be mistaken for sesame by the Villavecchia and Baudouin tests as at present printed in the A.O.A.C. book of methods. Prax' modifications of the Villavecchia test (C. A. 15, 3911) should be used with the Baudouin procedure. In the V. test it is only necessary to add 10 cc. of water and shake the reaction mixt. again if a doubtful pink appears, to remove any color due to substances present in pure olive oil. H. S. B.

Practical hints for oil refiners. J. P. HARRIS. *Cotton Oil Press* 6, No. 7, 27-8 (1922).—Edible oils contain non-fat compds., resins, coloring matter, etc., which, while present in small amts., greatly affect their quality. If these are not removed in refining they make the oil smoke at a low temp. and hasten rancidity. Refined oil should be filtered at as low a temp. as possible, kieselguhr being used. This will improve the bleach, give a soap-free oil and one which will not revert in color when deodorized. As little fuller's earth as possible should be used as it imparts a bad flavor to the oil. Carbons improve the taste by removing some of the disagreeable flavors. 350 to 375° F., the temps. usually employed in deodorizing, are too low to give good results. H. S. B.

New test for acrolein and its bearing on rancidity in fats. W. C. POWICK. *Ind. Eng. Chem.* 15, 66(1923).—The test described differs from the Kreis rancidity test in the use of H_2O_2 and of spectroscopic examn. The Kreis test, followed by spectroscopic examn., may safely be used to detect rancidity in *coltseeded oil*. E. SCHERUBEL.

Separation of solid and liquid fatty acids. W. MINGEN AND A. NEUBERGER. *Chem. Umschau Fette Oele Wachse u. Harze* 29, 337-42(1922).—Quant. detns. were made to test the accuracy of the methods for sepg. liquid from solid fatty acids. Mixts. were made of known amts. of stearic, palmitic, oleic, linolic, myristic and lauric acid, 2 or 3 acids being used in a mixt. The Varrentrapp method (based on the soly. of Pb oleate and linolate in Et_2O) extd. $\frac{1}{2}$ of the total oleic acid together with 5% to 10% of palmitic acid. The Farnsteiner method (soly. of Ph salts of the unsatd. acids in benzene) yielded liquid acids of I no. 81.4 and solid acids with an I no. of 4.5. The method of Bull and Fjellanger gave liquid acid of I no. 52.6 to 91.6, varying with the kind and amt. of acids used, and solid acids of I no. 15.9 to 38.3. David's method (insoly. of NH_4 salts of the solid acids in an excess of NH_3) extd. 0.953 g. of oleic acid a total of 1.003 g., with an I no. of 82 instead of 90, while the recovered stearic acid had a m. p. of 67° instead of 69° of the original acid. Niegemann's method (K salts in alc. KOH) was rejected on account of unreliable results. The method of Facchini and Dorta (K salts in acetone) yielded solid acids varying in I no. from 67.8 to 15.3 and liquid acids of an I no. from 90 to 84. M. and N. then tried sepn. with TI salts in 96% alc. and succeeded in sepg. stearic from oleic acid practically quant. They conclude that the Bull-Fjellanger, Facchini-Dorta and the David method yield approx. $\frac{1}{3}$ of the liquid acids in a pure condition. P. ESCHER.

New oil nuts from South America. ANON. *Bull. Imp. Inst.* 20, 147-52(1922).—*Mamarron nuts*.—In a previous investigation (C. A. 12, 1706) it was thought the palm producing mamarron nuts was probably *Scheelea excelsa*, Karst. (*Attalea excelsa*, Mart.); but it is now considered that it is nearer *S. insignis*, Karst. Nuts forwarded from the Magdalena valley in 1920 are stated to belong to a species of *Attalea* allied to *A. cohune*, Mart. The appearance of the whole fruit, nuts and kernels is described. The kernels contained 3.8% H_2O , and on extn. with light petr. ether yielded 69.9% of fat (equiv. to 72.7% on dry basis, 8.7% on nuts as received, and 7.9% on entire fruits) which was cream-colored, fairly hard, with an odor resembling that of coconut oil. Analysis gave: d_{20}^{25} 0.8679, m. p. 24.0° , m. p. of fatty acids 23.0° , acid value 2.3, sapon. no. 250.9, I no. 10.8, unsapon. matter 0.4%, sol. volatile acids 8.5, insol. volatile acids 10.8, n_D^{20} 1.449. The meal was cream-colored and had a pleasant taste resembling that of coconut meal. Analysis (calcd. to 7% fat) showed H_2O 12.6; crude proteins 22.4, fat 7.0, carbohydrates (by diff.) 41.3, crude fiber 11.7, ash 5.0%, nutrient ratio 1:2.5, food units 115. The meal contained no alkaloids nor cyanogenic glucosides. The oil should be suitable for the manuf. of margarine and other edible fats, and the meal as a feeding stuff. "*Fruta de Conejo*" (*Rabbits' fruit*), from the Magdalena Valley, belongs to a species of *Heisteria*, probably new. The appearance of the nuts and kernels is described. The sound kernels contained 5.4% H_2O , and on extn. with Et_2O yielded 61.2% of a clear, golden brown, viscous oil (equiv. to 64.7% on the dry basis and to 40.4% on the nuts as received), which gave on analysis: d_{20}^{25} 0.9940, m. p. of fatty acids below 10° , acid value 4.2, sapon. value 187.8, I value 140.0%, unsapon. matter 2.1%, sol. volatile fatty acids 0.2, insol. volatile fatty acids none, Ac value 128, n_D^{20} 1.502. On heating it decomposed suddenly at $250-285^\circ$ with evolution of copious fumes and formation of a carbonaceous residue. Prolonged heated at 200° for 4 hrs. gave a polymerized product resembling somewhat polymerized tung oil. Thin films of the oil, both pure and treated with PhO , did not dry on exposure to the air for 15 days. The cream-colored, tasteless meal gave on analysis (calcd. to 7% fat): H_2O 10.5, crude proteins

35.6, fat 7.0, carbohydrates (by diff.) 29.5, crude fiber 9.2, ash 8.2%, nutrient ratio 1:1.3, food units 136, cyanogenetic glucosides none, alkaloids trace. The oil might be suitable for making rubber substitutes and for soap-making. The meal has a high nutritive value; but owing to the presence of alkaloid practical feeding tests should be made. A. P.-C.

African oil palm nuts from Angola. ANON. *Bull. Imp. Inst.* 20, 152-4(1922).—Descriptions are given of the nuts of three varieties of the African oil palm (*Elaeis guineensis*), locally known as "Ehala," "Tundwa," and "Sombo," resp., which showed H₂O 6.5, 7.2 and 7.9, 7.5; oil (in kernels as received) 48.3, 51.7 and 48.4, 48.6; oil (in kernels on dry basis) 52.2, 55.7 and 52.5, 52.5; oil (in nuts as received) 10.8, 18.1 and 23.2, 10.6%. They are compared with "Abe-pa" and "Abobo-be" (palm nuts from Gold Coast) previously examd. (*Bull. Imp. Inst.* 7, 368(1909)). A. P.-C.

Oil of the Mexican poppy (Argemone mexicana). ANON. *Bull. Imp. Inst.* 20, 292-4(1922).—Seeds of *Argemone mexicana* from S. Africa contained 7.7% of H₂O, and on extn. with light petroleum ether yielded 36.5% of a limpid brownish yellow oil (39.5% on dry basis) with slightly acid odor, which showed: d_{4}^{15} 0.9220, n_D^{40} 1.466, solidifying point of fatty acids 22.8°, acid value 21.6, sol. volatile acids none, insol. volatile acids 1.16. The meal contained: H₂O 10.2, crude proteins 24.6, ash 7.7%. A thin film of the oil exposed to the action of air and sunlight was still slightly tacky after a week and had darkened considerably. Only slight improvement of the drying qualities was obtained by treatment with PbO and Mn dryers under various conditions. The only important com. use for the oil would be for soap making. It has purgative properties and the meal could not be used as a cattle food owing to the residual oil. A. P.-C.

Graphical calculation of (cotton) seed analyses. W. R. CRANDALL. *Cotton Oil Press* 6, No. 7, 36-8(1922).—A brief discussion of the theory of monograms followed by directions for making graphs. H. S. BAILEY

A few oil seeds from Indo-China. GEORGES CLOT. *Chimie et industrie* 8, 1122-4 (1922).—Walnut oil, "May-Chau" (*Carya tonkinensis*), gives nuts with 70.8% shell and 29.2% kernels. The shells contain H₂O 12.2, crude proteins 1.8, fiber 85.5, ash 0.5%. The kernels contain H₂O 6.09, fat 44.66, crude proteins 9.25, N-free ext. 35.30, crude fiber 2.95, ash 1.75%. The gasoline ext. is a fairly fluid, yellowish green oil, with slight green fluorescence, sapon. no. 201, I no. 96.5, Helmer no. 93, acid no. 58.9 (= 29.7% oleic acid), Ac no. 5. The fatty acids are liquid at room temp. Concd. H₂SO₄ gives first an orange, and then Madeira. H₂SO₄ and Ac₂O gives first a greenish brown, and then brown. Halphen's Br reagent gives no ppt. in 24 hrs. The oil consists mainly of glycerides of oleic, linoleic, and lower volatile or sol. acids, without any linolenic acid. The oil yield is so small that the nuts are of no com. value. Chestnut oil, "Mac Ken" (probably *Aesculus chinensis*). The ground nuts contain H₂O 8.45, fat 31.80, crude proteins 1.10, alc. (?) ext. 5.00, starchy material 36.15, crude fiber 14.70, ash 2.80%. The ext. consists of glucosides, saponoids, and reducing sugars sol. in alc. The oil obtained has a slightly acid taste, and is pale yellowish brown. On cooling, tristearin seps. out, identified by its m. p. and sapon. no. Above 40° it is quite homogeneous; d_4^{20} 0.8909, sapon. no. 230, I no. 64.2, Helmer no. 92, acid no. 42.5 (= 21.4% oleic acid), titer test of the fatty acids 43°, I no. of liquid fatty acids (via Tortelli) 88, Ac no. 0, hexabromides none. This shows the presence of sol. acids of low mol. wt. and absence of linolenic and hydroxy acids. Oleic acid is the only unsatd. acid. The oil contains about 70% of triolein and 20% of tristearin. The fat-free meal could be washed with cold water to remove the saponins, heated 5 min. with water under pressure to 105° to swell the starch grains, treated with malt, and fermented. *Paranephelium* contained 28.8% of easily sepd. shell and 71.2% of kernels. The former gave: H₂O 12.50, fat

1.20, crude proteins 2.40, alc. (?) ext. 14.20, crude fiber 67.20, ash 1.50%. The ground kernels gave: H_2O 5.40, fat 57.60, crude proteins 11.60, starchy materials 16.30, crude fiber 6.60, ash 2.50%. A cyanogenetic glucoside is present. The gasoline ext. is a light yellowish orange oil, remains clear at 20° , sapon. no. 227, Hehner no. 64.5, I no. 92.7, acid no. 2.1 (=1.1% oleic acid), unsapon. matter 0.46%, av. mol. wt. of fatty acids 292, titer test of fatty acids 39° , I no. of unsatd. acids (via Tortelli) 89, Ac no. none, hexabromides none; H_2SO_4 gives a yellow color turning brownish, Ac_2O and H_2SO_4 , no coloration at first and then slight greenish blue. It contains a substance yielding NH_3 during sapon. and HCN on treatment with acids. It contains about 70% of triolein and glycerides of lower and sol. acids.

A. P.-C.

Determination of the mixture of arachidic and lignoceric acids in peanut oil by means of magnesium soaps. A. W. THOMAS AND CHAI-LAN YU. *J. Am. Chem. Soc.* **45**, 113-28(1923).—The following soly. detns. (g. per 100 cc. of soln.) at 25° in 91.53, 86.16 and 63.07% alc. (by wt.) were made: stearic acid 1.803, 1.014, 0.087; lignoceric acid 0.182, 0.092, 0.011; Mg stearate 0.006, 0.006, 0.005; Mg lignocerate 0.005, 0.005, 0.006; Mg oleate 6.64, 5.35, 3.89. K salts (in 91.53% alc.): stearate 0.483; lignocerate 0.123; oleate 25.2. Pb salts in Et_2O : stearate 0.015; lignocerate 0.018; oleate 6.46. A new method, based upon the above soly. detns., for the quant. detn. of peanut oil is proposed; it has the following advantages: (1) The const. errors, such as are involved in the solubilities of the Pb soaps in Et_2O , are reduced to a min.; a direct and more rapid sepn. of satd. and unsatd. acids in peanut oil is accomplished without the use of a second solvent; higher % yields of arachidic and lignoceric acids than those from the "Ph salt- Et_2O " method are obtained; common vegetable oils, including cold drawn cottonseed oil, do not interfere with the quant. detn. of peanut oil at either 20° or 25° . The method is not intended for the sepn. of satd. from all unsatd. acids in all fatty oils, as Mg erucate and an unsatd. soap from tung oil (probably eleostearate) are insol. in 90% alc. (by vol.) (see following abstr.). The soln. left after the detn. of the sapon. no. may be utilized for the sepn. of the mixt. of arachidic and lignoceric acids by the proposed method, affording an excellent qual. and fair quant. method for identifying peanut oil. The method is briefly as follows: About 10 g. of the oil is sapond. with alc. KOH, treated while still warm with alc. AcOH and then with alc. KOH until it gives a permanent pink color with phenolphthalein, treated with 25 cc. alc. $Mg(OAc)_2$ (50 g. salt in 400 cc. alc.), heated jst to boiling and allowed to stand overnight at about 10° ; the resulting insol. Mg soaps are boiled 5 min. with 100 cc. of 5 M HCl and after a few min. slowly treated with cold H_2O ; the pptd. acids, after being washed free from Mg and Cl ions, are allowed to stand overnight in 60 cc. alc. at 29° or 25° ; the crystals which sep. are washed with 90 and then with 70% alc. (the vol. of the filtrate and the 90% alc. washings being noted), dissolved in abs. alc. and evapd. and dried to const. wt. at 80° in a weighed flask, the wt. found being corrected for the amt. of arachidic and lignoceric acids remaining in the filtrate and 90% alc. washings. The mixed acids so obtained m. $71-3^\circ$, contain no ash, have no I no. and have a mean mol. wt. of about 340; after another recrystn. from 90% alc., they m. $75-6^\circ$. The method, applied to Spanish, Texas, Java, Virginia, Alabama, Mexican and China crude peanut oils, gave 5.17-5.48% total acids; five refined oils gave 4.79-5.13% acids. The Pb salt- Et_2O method with 3 of the above crude oils gave 4.75-5.37% acids.

C. A. R.

New qualitative tests for rape and tung oils. A. W. THOMAS AND CHAI-LAN YU. *J. Am. Chem. Soc.* **45**, 129-30(1923); cf. preceding abstr.—In developing the quant. method for the detn. of peanut oil it was found that of the solid acids resulting from the decompn. of the Mg salts obtained from rape oil only a small amt. (less than 0.5%) was insol. in 90% alc. at 20° and none at 25° . Two samples of genuine rapeseed oils, treated like the peanut oils as described in the preceding abstr. except that the acids

from the decompd. Mg salts were allowed to stand in 90% alc. at 20° or 15° instead of 25°, filtered from any crystals which might have sepd. and evapd. to dryness, gave about 25% of an acid m. 35°, mean mol. wt. about 328°, I no. 70-2; it is believed to be erucic acid. The Mg soaps from all oils examd. (preceding abstr.) are entirely or almost entirely sol. in boiling alc. with the exception of tung oil which yields an abundance of a white elastic Mg soap insol. in 90% alc. even on prolonged refluxing; the acid liberated from this insol. Mg salt has the strong odor characteristic of tung oil, is sol. in cold 90% alc., m. about 44°, absorbs O from the air and changes to a dark brown resinous mass in 1-2 days. It is believed to be eleomargaric acid. The yield from one sample of tung oil tested was about 20%. C. A. R.

Solubility tests of castor oil. H. P. TREVITHICK AND M. F. LAURO. *Cotton Oil Press* 6, No. 7, 32-3(1922).—If castor oil dissolves in EtOH under the conditions of the U. S. P. or other standard test it is probably pure but it should not be condemned as impure solely because it does not. Analyses of 4 samples of castor oil which did not pass the Finkener test (10 cc. of sample completely sol. in 50 cc. of EtOH ($d_{15.5} 0.829$)) are tabulated. The acetyl values 145 and 148 indicate that certainly 2 of these were pure. Pure castor oils which when fresh were completely sol. in 90% EtOH in 10 mos. changed so they gave a turbidity in this reagent although stored in closed cans. Concordant results on the acetyl value of castor oils could not always be obtained by the filtration method. The distn. procedure did give very concordant results, especially when H_3PO_4 instead of H_2SO_4 was used to acidulate before distn. Method is given in detail. H. S. BAILEY

Irvingia Smithii. J. PIERAERTS. *Mol. grasses* 14, 6303-4(1922); cf. C. A. 16, 1672.—The carefully cleaned nuts consisted of 84.75% shell and spermoderm and 15.25% kernel. Wt. of one nut 11.02-14.90 g., av. 13.12 g. Shells (8.44% moisture) contain (on dry basis): total ash 0.55, water-sol. ash 0.30, total N 0.20, crude protein 1.25, P_2O_5 0.027%; alky. of ash (as K_2CO_3) = 50.98% of total ash and 92.68% of water-sol. ash. Kernels (3.80% moisture) contain (on dry basis): total ash 2.28, water-sol. ash 0.96, total N 1.26, crude protein 7.88, fat 75.03, P_2O_5 0.34%, alky. of ash (as K_2CO_3) = 10.77% of total ash and 39.92% of water-sol. ash. The fat extd. with cold petr. ether b. below 50° gave: m. p. 37.8-39°, solidifying point 36.8-36.4°, acid no. 7.1 (=3.55% oleic acid), sapon. no. 237.3, I no. 2.96, sapon. no. of acetylated fat 248, Ac no. (via E. André) 13.01, Crismer no. (carried out in sealed tube on 1 vol. of fat and 2 vol. of 99.8% alc.) 37°, Halphen test negative; solid fatty acids gave m. p. 33.9-36°, solidifying point 32-29.8°, neutralization no. (cold) 264.5 (=av. mol. wt. of 212.2), sapon. no. (hot) 264.5, I no. 3.03, Halphen test negative, alkaloids none, cyanogenetic glucosides none. The fat should be quite suitable for high grade soaps, edible fats, etc.

A. P.-C.

Cane and berry wax. M. RINDL. *S. African J. Ind.* 5, 513-8(1922).—Cane wax is a white powdery substance found on the surface of the stalk of the sugar-cane. It is obtained by passing the cane through a tank through which hot H_2O is passed in the opposite direction or by skimming the surface of the sap. The wax extd. from cane with benzine, m. 55°, solidifies 51°, $d_{15.5} 0.968$, acid no. 38.6, sapon. no. 167.9, ester no. 129, Hehner no. 88.6, R.-M. no. 7, I no. 60, unsapon. 27.7%, glycerol 7.2%, ash 2.03%, lecithin 2.7%, N 0.15%. The wax has been used to a limited extent in the polish and elec. industries for gramophone making, and as a substitute in other industries, for carnauba, bees, and montan wax. Berry wax is obtained from different species of *Myrica* or myrtle. Strictly speaking the material is not a wax but a vegetable fat. Five samples varied as follows: m. 40.5 to 45°, $d_{15.5} 1.004$ to 1.007, sapon. no. 211 to 214.6, I no. 0 to 2.38, acid no. 4.08, mean mol. wt. of fatty acids 236.1, m. p. of fatty acids 47.5°. Its principal use is for the manuf. of candles and for the adulteration of

beeswax. It gives a splendid quality soap of white color, but the price is prohibitive.

E. SCHERUBEL

Standard methods for the sampling and analysis of commercial soaps and soap products. ARCHIBALD CAMPBELL, *et al.* *J. Ind. Eng. Chem.* **14**, 1159-63(1922).—The committee on methods of analysis and specifications of com. soaps and soap products of the Division of Industrial Chemists and Chemical Engineers of the Am. Chem. Soc. adopted methods Apr. 3, 1922 which can be directly applied to com. transactions, and are believed to be as accurate as economic considerations warrant. E. SCHERUBEL

Color measurement for oils. F. E. BAKER. *J. Ind. Eng. Chem.* **14**, 1169(1922).—Polemical against Parsons and Wilson (*C. A.* **16**, 1660). Reply by PARSONS. *Ibid* 1169-70.

F. SCHERUBEL

Influence of physical characteristics of fuller's earth on its bleaching power. A. W. PUTLAND. *Cotton Oil Press* **6**, No. 7, 34-5(1922).—The bleaching value of fuller's earth on vegetable oils is independent of its chem. compn.; it depends entirely upon its selective absorption. The coloring matter is retained in the pores of the earth and therefore it should be ground to a fineness that will expose a max. number of these pores without rupturing them. Curves are given showing the relation of bleaching value to fineness, sp. gr. and moisture. The bleaching power increases rapidly with fineness up to 150-mesh. The oil absorption increases and the bleaching power decreases as the sp. gr. decreases. As the absorbed water is removed from fuller's earth its power to remove coloring matter from oils increases but if the earth be heated sufficiently to remove the H_2O of compn. it may be ruined. This is due to the change of hydrated silicic acid into the anhyd. form.

H. S. B.

Colloid chemistry of soap. II. The soap boiling processes. J. W. MCBAIN AND ERNEST WALLS. 4th Report, *Brit. Assoc. Advancement of Sci.* **1922**, 244-63; cf. *C. A.* **15**, 1412.—This paper includes 3 sections: (1) actual soap boiling practice, (2) theory of soap boiling and semi-tech. expts. and (3) applications of theory. Under (1) are included 1st change ("killing," pasting, sapon., empâtage), 2nd change (graining, salting out, relargage), 3rd change (washing), 4th change (strengthening change, boiling on clear boiling, coction), 5th change (fitting, settling, liquidation. Under (2) are included historical review, general review, hydration of the fibers in soap and, bearing on emulsoid theory of colloids, conditions for the formation of 2 liquid layers. Under (3) are included sapon., graining and washing, fitting and settling, color and hardness of soaps. The color of com. soaps is due to impurities, chemically pure soaps being colorless. Whiteness and hardness are favored by satd. fatty acids whose Na salts are insol. at room temp. Localized equilibria are the rule in soap; therefore drying alters the surface and form of bars of soap in a rather more complicated fashion than with ordinary gels. Long exposure to air carbonates free alkali in soap, making such soaps more transparent, for hydroxide makes the curd fibers less sol. than does carbonate. Slowly cooled (framed) soaps are relatively soft and translucent because of segregation. Chilled soap shows no visible structure, is more opaque, harder and devoid of luster.

JEROME ALEXANDER

Colloidal chemistry and the soap industry. F. ENGEROFF. *Kolloid Z.* **31**, 301-3 (1922).—An address.

E. SCHERUBEL

Animal oils, fats, and waxes. (I). (II). Oils. C. F. JURITZ. *S. African J. Ind.* **5**, 438-44, 506-12(1922).—The general information available on sea and land animal oils is given.

E. SCHERUBEL

Cold-made filled toilet soaps. I. P. *Seifensieder Ztg.* **49**, 747-8(1922).—The faults of cold-made filled soaps are enumerated. Five formulas for coconut oil soaps are given.

P. ESCHER

The olive and olive oil (BONNETT) 12. Oxidizing liquid hydrocarbons (U. S. pat. 1,436,136) 22.

Composition for refining vegetable oils. Z. OLSSON. U. S. 1,485,972, Nov. 21. A compn. adapted for bleaching and filtering cottonseed oil or other oils is prepd. by beating to 700° or higher a mixt. of calcined bauxite 75, starch 20 and bentonite 5%.

Soap. A. O. ZINK. U. S. 1,436,928, Nov. 28. Pellets of toilet soap are coated with a thin layer of sugar, shellac or other readily broken material to prevent drying out before use. U. S. 1,436,929 relates to toilet soap mixts. in sheet form and of pliable tenacious character, e. g., a mixt. of soap, gum acacia or dextrin and glycerol.

Wooden frames for soap-cooling apparatus. C. W. COUCHE and J. KENYON. U. S. 1,437,339, Nov. 28.

28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

Invertase process of manufacturing sugar. J. K. DALE and C. S. HUDSON. *Am. Food J.* 17, No. 8, 27-9(1922).—The process using invertase by which a rich heavy cane-sugar sirup can be manufd. is explained in detail. H. A. LEPPE

The nipa palm as a source of sugar and alcohol. ANON. *Bull. Imp. Inst.* 20, 315-25(1922).—A description of the occurrence and habits of the nipa palm (*Nypha fruticans*, Thunb.), and of the method used in the Philippines for the collection of sap and production of sugar and of alc. A. P.-C.

The Kauri-gum industry of New Zealand. ANON. *Bull. Imp. Inst.* 20, 331-7(1922).—Description of the methods used for recovering kauri-gum. A. P.-C.

Clarifying cane juice. M. BIRD. *Facts About Sugar* 16, 12(1923).—Muller's method of heating juice to 241° F. before liming was used with good results in improving clarification by removing the restraining influence of silica. About 65% of the lime used in ordinary clarification is required when the juice is heated, as above, before liming. N. KOPPELOFF

The iodometric determination of sugar (AUERBACH, BODLÄNDER) 7.

Zucker, aus dem Ergänzungsbande. IV. Zu Muspratt's "Encyclopäid. Handbuch der Technischen Chemie." Braunschweig: Fr. Vieweg and Son. Reviewed in *Deut. Zuckerind.* 47, 212(1922).

29—LEATHER AND GLUE

ALLEN ROGERS

Ing. Josef Jettmar. ANON. *Gerber* 1922, 177-8; *Cuir* 11, 532(1922).—Obituary. F. L. SEYMOUR-JONES

Art and science of leather manufacture. I. F. L. SEYMOUR-JONES. *Chem. Met. Eng.* 27, 1110-4(1922); II, *Ibid* 1253-8.—General descriptive articles from a scientific standpoint, covering sources and kinds of skins, flaying, preservation, disinfection and cure, structure and chem. nature of skins, and the preliminary network. F. L. SEYMOUR-JONES

The adsorption of alkali by animal hide and the effect of formaldehyde thereon. O. GERNGROSS and H. LOEWY. *Collegium* 1922, 229-47; cf. *C. A.* 16, 1335.—An app. was devised for the shaking and filtering of hide powder with alk. solns. in absence of

atm. CO_2 . With this the amt. of alkali adsorbed by hide powder, treated and untreated with HCHO , was studied for isohydric solns. of KOH , NaOH , $\text{Ba}(\text{OH})_2$, and $\text{Ca}(\text{OH})_2$. The amt. of alkali adsorbed was estd. by titration of the residual liquor. With untreated hide powder a completely reversible equil. was reached in 2 mins., yielding the common Freundlich adsorption isotherm. In isohydric solns. the adsorption was in the order $\text{Ba} > \text{Ca} > \text{Na} > \text{K}$. The presence of KCl increased the adsorption of KOH . With the HCHO treated hide powder about 1 hr. was necessary for equil., being the more rapid the more dil. the alkali solns. Adsorption of alkalies was considerably increased by the treatment, and the adsorbed alkali showed greater resistance to washing out. Care was taken to obviate errors arising from the possible formation of HCOOH from the HCHO . In conjunction with the fact that HCHO treatment diminishes the acid adsorption of hide powder, these results favor the view that a chem. reaction occurs between the HCHO and the basic groups of the hide protein. F. L. S.-J.

The colloidal state of matter—colloid chemistry in the tanning industry. I. H. BOAS. *Chem. Eng. Mining Rev.* 15, 31-2(1922).—A brief summary of a lecture before the Melbourne Univ. Chem. Soc., describing the great advances made in quant. leather chemistry by the investigations of H. R. Procter and his collaborators and of Jacques Loeb on the physical chemistry of the proteins. The Procter-Wilson theory of vegetable tanning has been successfully applied to practice; by controlling the p. d. between the hide protein and tan liquor as indicated by the theory, the rate of tanning and nature of the tannage can be controlled. Emphasis was laid upon the importance of H-ion control and the significance of the isoelectric point of the hide protein. J. A. WILSON

Preservation of fur skins. P.-U. COURAUD. *Cuir* 11, 513(1922).—The fresh and well flayed skins are thoroughly washed, and all muck, fat, blood, etc., removed. They are then brushed over on the flesh side with a mixt. of soft soap 48%, hard soap 48%, and arsenious acid 4%, and dried in the shade. The hair side is then brushed to clean it, and again brushed over with a 0.1% alc. soln. of HgCl_2 . F. L. S.-J.

The points of minimum plumping of calf skin. J. A. WILSON AND A. F. GALLUN, JR. *Ind. Eng. Chem.* 15, 71-2(1923).—The curve representing the plumping of unhaird and purified calf skin as a function of p_H value has 2 points of min., the one of lower value occurring at about 5.1, the other at about 7.6. It is suggested that these 2 points indicate the isoelectric points of 2 forms of the protein of calf skin. J. A. WILSON

The plumping of hide powder by lactic and acetic acids. J. S. ROGERS. *J. Am. Leather Chem. Assoc.* 17, 611-22(1922).—Clafin's method (*C. A.* 14, 2730) for detg. the plumping power of solns. was found to be workable. Solns. of lactic and acetic acids cause hide powder to swell to the same extent at the same H-ion concn., but not at the same normality of acid. The presence of tannin lowers the plumping effect produced by these acids. The terms *plumping* and *swelling* are used synonymously. J. A. WILSON

Analysis of synthetic tanning materials—1922 committee report. T. A. FAUST, et al. *J. Am. Leather Chem. Assoc.* 17, 622-38(1922).—Attempts to differentiate between sulfuric and sulfonic acids were unsuccessful. It is hoped to develop methods for detg. HCHO and free H_2SO_4 and whether a given syntan contains an excess of acid that would be injurious to leather. J. A. WILSON

Analytical contribution to the study of (French) colonial tanning materials: Vegetable tanning materials from Tonkin. L. TARDIVOT. *Cuir* 11, 516-8(1922).—Analyses were made of various tanning materials from Tonkin (French Indo-China). Mangrove bark (5 samples) yielded from 15.33 to 28.78% tans and 6.60 to 10.02% non-tans. Gié bark (chiefly cupulifers, oaks, and castanopsis—9 samples) gave 3.36 to 19.25% tans and 1.50 to 5.90% non-tans, giving a rapid tannage and a brownish red, empty leather. Soi bark (chiefly oaks and castanopsis—3 samples), 7.36 to 20.04% tans, 2.40

to 3.60% non-tans; gives a slower tannage and a firm leather of color like chestnut-tanned. A dozen other different specimens of indigenous barks, woods, leaves, fruits and galls were analyzed, yielding up to 11.4% tans. The possibility of establishing an ext. industry is offset by the scattered nature of the trees. Intensive cultivation on a large scale is essential as a preliminary.

F. L. SEYMOUR-JONES

Time reduction in the tanning process. R. O. PHILLIPS. *J. Am. Leather Chem. Assoc.* 17, 594-605(1922).—A general review of well known methods for decreasing the time required for vegetable tanning.

J. A. WILSON

Synthetic tannins. D. KOPP. *Gerber* 1922, 178-80.—A general description.

F. L. SEYMOUR-JONES

Studies of the strength of proteolytic enzymes in the process of bating. C. S. HOLLANDER. *J. Am. Leather Chem. Assoc.* 17, 638-47(1922).—Large-scale expts. were conducted on the bating of skin by both dung bates and pancreatic enzymes. Detn. of the tryptic activity of the bate liquors by the Sherman-Neun method gave uniform results during the progress of bating with the enzyme prepn., but erratic results where dung infusions were used.

J. A. WILSON

BOGUE, ROBT. H. *The Chemistry and Technology of Gelatine and Glue*. New York and London: McGraw-Hill Co., Inc. 30s. 640 pp. Reviewed in *Can. Chem. Met.* 6, 227 and *Engineering* 114, 623(1922).

Leather-like product. H. W. MORGAN. U. S. 1,436,106, Nov. 21. A leather-like material is prepd. by treating fibrous material such as wood flour, rags, straw, grass or jute with a softening bath, e. g., hot NaOH soln., and then with HOAc, allowing the product partially to set after adding varnish gum soln. and then compressing and solidifying it and curing it by hot air currents. The material thus obtained is suitable for use in the form of sheets which may be colored or embossed. U. S. 1,436,107 relates to a similar process in which coloring agents are added before the product prepd. has set.

Unhairing skins and hides. W. RAUTENSTRAUCH. U. S. 1,435,876, Nov. 14. A depilating compn. is prepd. by adding hide substance to an aq. Ba(OH)₂ soln. until no more will dissolve. This soln. does not cause loss of wt. of hides treated.

30—RUBBER AND ALLIED SUBSTANCES

J. B. TUTTLE

The presence of quebrachitol and sugar in Hevea latex under different circumstances. W. SPOON. *Arch. Rubbercultuur* 6, 269-87(1922).—The reduction of Fehling soln. does not give exact figures for the sugar detn. of the latex. S. uses the rotatory power; three distinct groups of substances, contained in the latex, deviate the plane of polarization: quebrachitol, sugars and proteins. The sp. rotatory power of quebrachitol is known. The following method is employed to remove the proteins: The latex is first coagulated by adding 1/2 vol. of AcOH (2 1/2% soln.); a part of the serum, thus obtained, is mixed with an equal vol. of 96% alc. which ppts. all proteins. After filtering off the ppt. the rotatory power is detd. which corresponds to the difference of the deviation of quebrachitol and sucrose (=q-s). Another definite vol. of the serum is boiled with HCl to cause inversion, and the deviation of polarized light is again detd. which equals q + i, where i is the deviation of glucose + fructose. As the ratio of the sp. rotatory powers of sucrose : glucose + fructose is known to be s:i = 17:5, the calcn. of q from the data obtained above is possible.

R. BEUTNER

The knowledge of the sugars present in the Hevea latex. L. R. VAN DILLEN.

Arch. Rubbercultuur 6, 623-8(1922).—Investigations were performed with the dialyate of the latex. Only after inversion was it possible to trace sugars by means of their reducing power with Fehling soln. The inverted dialyate was treated with phenylhydrazine sulfite. In this way the glucosazone and the galactosazone could be isolated. The latex most likely contains heterosaccharides, the products of decompn. of which are either glucose or fructose or these sugars together and galactose. R. BEUTNER

Individual differences in the starch contents of *Hevea brasiliensis*. T. SCHWEIZER. *Arch. Rubbercultuur* 6, 209-19(1922).—In the course of 2 yrs. the changes in the starch content of the bark of *Hevea* were studied during wintering. Three cases of starch mobilization in the bark of *Hevea* were distinguished: (1) some trees, while forming leaves, first dissolve the starch of the bark of the higher roots; (2) mobilization of the starch in the root and the stem at the same time; (3) mobilization first in the upper parts and later in the root. Further individual differences in the starch contents of *Hevea* appeared in the regeneration of the bark and in tapping. When a tree is tapped under such conditions that the flow of latex is prevented, there is only a consumption of bark. In some cases a disappearance of starch could be noted over a great area, but in other cases the starch remained unaltered. The trees yielding best gave a minimal consumption of starch. Therefore, the theory cannot be accepted that there is a direct relation between the disappearance of starch by intense tapping and the formation of rubber. R. BEUTNER

The connection between starch content and tapping off the latex. J. SCHWEIZER. *Arch. Rubbercultuur* 6, 327-34(1922).—The starch content allows one to judge the state of growth of a tree; with a moderate tapping off the starch content remains unaltered. R. BEUTNER

Coagulation with acetic acid. H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 4, 660-2(1922).—A review of the results of Parkin, Morgan, Whitby, and de Vries with reference to the amt. of AcOH required for the coagulation of latex in different conditions. G. S. W.

Internal mixers. R. P. DINSMORE. *Chem. Met. Eng.* 27, 890-3(1922).—In the rubber industry internal mixers have been used successfully on low-grade stocks (lower proportion of rubber content). They save labor and reduce dust and fumes as compared with roll mixers. On high-grade stocks the higher temps. produced by internal mixers are apt to cause scorching and a tougher mix. The article displays a cross section of the Birmingham-Banbury mixer and an illustration of same together with a cut showing the Farrel masticator and a standard mixing mill. A. C. LANGMUIR

The aging of some previously tested samples. H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 4, 662(1922).—The samples referred to in C. A. 16, 4363, behaved similarly on aging for 72 and for 144 hrs. at 70°. G. S. W.

Aging of rubber prepared with sodium fluosilicate. H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 4, 662-4(1922); cf. C. A. 17, 481.—The tests reported indicate that rubber prepd. from latex to which Na_2SiF_6 has been added age at least as well as rubber prepd. without such addition, and that the use of excessive proportions of Na_2SiF_6 has no prejudicial effect on the aging. G. S. W.

Some investigations in connection with the fight against Black Thread. P. F. KEUCHEMUS. *Arch. Rubbercultuur* 6, 403-8(1922).—Numerous disinfectants are compared as to their fungicidal action: Izal, Bacerol, Soccin, Noxonin, Phenyl, Creoline, Jeyes fluid, Coeff. 2, Coeff. 18/20. A 3% soln. of Izal is found to be the most effective if applied daily after tapping; unslaked lime improves its fungicidal strength. No details are given concerning the chem. compn. of the substances used. R. BEUTNER

A coloring matter for disinfectants in the treatment of the Black Stripe disease. L. R. VAN DILLEN and JOHANNES GANDRUP. *Arch. Rubbercultuur* 6, 220-5(1922).—

Most of the prepus. used for treating "Black Stripe" cannot be seen easily when applied to the tapped surface. When fuchsin is added to the dil. disinfectant, the tapped surface shows a red band easily visible; the color of this is not lasting, however. The fuchsin has no influence on the rubber.

R. BEUTNER

Rubber vulcanization accelerator. P. I. MURRILL. U. S. 1,436,894, Nov. 28. Rubber compds. are vulcanized with the assistance of an oxidation product of an insol. salt of a secondary amine, previously condensed with CS₂, *e. g.*, the Zn or Cd salt of dimethyldithiocarbamic acid.

